

Current Status of EPA Office of Mobile Source
Air Pollution Control Characterization
Projects: Summary

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Summary of Current Status of
EPA Office of Mobile Source Air Pollution Control
Characterization Projects

Thomas M. Baines

August, 1981

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I. Overview

The Characterization Program of ECTD has focused on expanding the knowledge of pollutants as they are emitted from various mobile sources. This work has been done within ECTD, by in-house and extramural programs, as well as monitoring the characterization efforts performed by other organizations both within EPA and by industry and others. Some of the principal guiding objectives of the ECTD characterization program can be summarized by the following points.

1. The characterization of pollutants not normally tested and that may represent a human health concern.

Currently, and in the past, a large amount of effort has been expended by industry and EPA characterizing the hydrocarbon, carbon monoxide and oxides of nitrogen emissions from a variety of engines and vehicles. However, there may be other compounds being emitted by vehicles that may be hazardous. Especially of interest would be those compounds that may have a deleterious effect on human health. Some of these compounds would be emitted in varying amounts from uncontrolled as well as controlled engines. Other compounds (such as catalyst attrition products) could be emitted mostly from vehicles which have emission control systems designed to lower HC, CO and NOx. Various systems to improve both emissions and fuel economy could have a large impact on unregulated emissions. Since motor vehicle technology is changing so rapidly now in response to the need for improved emissions and fuel economy, it is critical that ECTD characterize new systems for unregulated pollutants. Consequently, the ECTD program has been focused on characterizing a broad range of compounds from present and future engine and vehicle technologies.

2. Testing for a variety of pollutants under malfunction conditions.

Much, if not most, of the testing performed by EPA and other laboratories has been done with the engines tuned to manufacturers' recommended specifications. However, many vehicles that are in use today operate under conditions of tune that do not meet the manufacturers' recommended specifications. This could result in increased emissions of a variety of both regulated and unregulated pollutants, some of which could have negative human health effects. As a consequence, ECTD has tested a variety of engines/vehicles for pollutants of concern under malfunction conditions to estimate the impact that such vehicles/conditions would have on the environmental loading of pollutants.

3. Fuel parameters.

The fuel situation in the United States is currently very dynamic, in that we are rapidly developing alternate sources of fuel to supplement conventional petroleum sources. These alternate sources include lower grade petroleum crudes, as well as alternative and synthetic fuels derived from coal and oil shale. Some of the new fuels will be alcohols including methanol. These newer fuels may have a dramatic effect on emissions and, as such, ECTD has performed some characterization on these emissions as well as remained abreast of the field in general. Also, some testing has been done on emissions from Diesel vehicles, as these emissions may be impacted by fuel parameters. The ECTD fuels characterization program will continue in an effort to more fully characterize the future fuels. This work is of critical importance in that it helps assure that alternate fuels are environmentally acceptable. One can probably tailor fuel composition and processes to obtain maximum environmental benefit from these fuels if one does this characterization before these fuels are widely produced.

4. Characterization of pollutants from engines/vehicles that are involved in a transition environment.

There are many engines/vehicles that are involved in a transition environment created by various regulatory initiatives, fuel economy incentives, etc. ECTD is very interested in characterizing the emissions from these vehicles/engines to be able to evaluate the impact that this transition may have. For example, the heavy-duty Diesel engine manufacturers are now currently changing many of their engines from the traditional, naturally aspirated type over to the turbocharged type. In an effort to evaluate this change and how it affects pollutants, some testing has been done on equivalent engines. Also, there is currently a trend towards Dieselization of both the light-duty fleet as well as the mid-range heavy-duty fleet. Comparative application engines for both of these fleets have been tested so that an estimate can be made of how such a change will impact the environmental loading of pollutants. Also, a variety of other technologies have been evaluated so that their influence can also be estimated. These include the influence of indirect injection in a heavy-duty Diesel engine, the influence of high pressure injection in a Diesel engine, and others.

With these objectives in mind, a variety of programs and projects have been performed. The more recent and more important of these projects are summarized in the following section.

II. Summary and Conclusions

EPA-OMSAPC is conducting a thorough characterization of unregulated emissions on a variety of current and prototype engines. Extensive work is also underway to see how various fuel parameters affect regulated and unregulated emissions. This latter work includes projects on alternate fuels such as methanol as well as fuels derived from coal or oil shale.

Based on the recent work the following conclusions can be made.

1. The effects of a number of engine parameters on regulated and unregulated emissions were examined for several heavy duty Diesel engines. It was found for two Daimler-Benz engines that turbocharging generally decreased all emissions with the major exception being NOx, for which a slight increase was noted.

It was found on a Caterpillar 3406 engine that advanced injection timing increased HC, CO, NOx, sulfates, and aldehydes while reducing particulates and extractable organics. It was found on a Caterpillar 3406 engine that changing from a direct to an indirect injection system increased HC, brake specific fuel consumption, and sulfates but decreased CO, NOx, particulates, organic extract, and odor. With a Mack ETAY(B) 673A engine, water injection (30% volume) was found to reduce NOx slightly, increase HC and CO slightly, but increase particulates and extractable organics greatly.

Different fuel pumps and the effect of EGR on regulated and unregulated emissions were also examined. The use of a high pressure pump reduced particulates greatly but increased NOx. Use of EGR decreased NOx but increased particulates.

2. The soluble organic emissions from four different heavy duty Diesel engines were compared with those from a heavy duty gasoline engine burning leaded fuel. The Diesel engines showed a higher percent of organic extractables from the particulate than the gasoline engine. The percent extractables decreased greatly as load increased for the Diesel engines.

Also, the gasoline engine was compared to a Diesel used in similar applications. The Diesel engine had much lower HC and CO with slightly higher NOx emissions. The Diesel emitted a much higher quantity of particulates and percent extractables but had somewhat lower BaP emissions. Sulfate emissions were greater but aldehydes were less for the Diesel engine.

3. Limited testing has been done on Diesel bus engines under malfunction conditions which would simulate emissions under in-use conditions where engines are frequently not tuned up to manufacturers' specifications. The one engine tested so far shows an increase in HC, CO, brake specific fuel consumption, and a large increase in both particulates and extractable organics. A second engine is being tested.
4. Work has been done comparing emissions from an Oldsmobile and VW Diesel with their gasoline counterparts. These tests showed generally higher HC, much higher particulates, higher BaP, higher sulfates but lower CO from the Diesel versions. There was no clear trend with aldehydes although the aldehydes were usually higher with the Oldsmobile Diesel versus gasoline engine.
5. EPA has conducted extensive tests on four oxidation and four three-way catalyst equipped gasoline vehicles under malfunction conditions. The malfunction conditions tested include rich-best-idle, 12% misfire, disabled EGR, higher oil consumption, and faulty air injection. Both the oxidation and three-way catalyst-equipped vehicles generally showed higher regulated and unregulated emissions.

These results were compared with data from a non-catalyst equipped vehicle.

It appeared as though sulfate, ammonia, and nitrous oxides were higher from catalyst equipped cars than from the one non-catalyst car. Hydrocarbons and aldehydes were highest from the non-catalyst car. Ammonia and cyanides were highest from the three-way catalyst cars. It

appeared that the unregulated exhaust emissions composition from catalyst equipped cars operating under malfunctioning conditions was, in general, distinguishably different from that of the non-catalyst cars.

6. EPA has also conducted a program to examine how Diesel fuel parameters affected emissions from typical light duty Diesels (a VW and Mercedes Benz 240D). Five different Diesel fuels were tested. It was found that the minimum quality fuel frequently adversely affected emissions. A follow-on project was conducted in which very specific fuel parameters were varied to determine their effect on emissions. This work showed that phenol emissions were strongly affected by the shale oil blend.

Particulate rates were reduced with the fuel containing the light-end blend and the olefin blend, by 14 percent and 6 percent, respectively. The two blends containing aromatics were associated with increases in particulate emissions of about 27 percent. The cetane-improved aromatic fuel blend increased particulate emissions about 68 percent over those observed with base fuel. Heavy ends fuel apparently did not cause an increase in particulate emissions. Also, blends containing aromatics resulted in slightly less organic solubles extracted from the particulate matter. Olefins, light ends, and heavy ends of fuels were associated with increases in the amount of organic solubles.

7. EPA has just started a program to investigate how alternate fuels (including fuels derived from coal and oil shale) affect emissions. Four fuels (a #2 Diesel fuel, #2 Diesel fuel marine from oil shale, a Paraho JP-5 from oil shale, and a Coal Case 5A fuel (a fuel containing solvent refined coal (SRC II) and petroleum materials blended by the U.S. Army)) are being tested with a VW Diesel. There was virtually no change in HC, CO and NOx emissions with the shale marine fuel. This was also true of the particulate emission rate. The aldehydes, however, decreased slightly. The phenols stayed much the same, as well as the odor. There was a slight increase in the fuel economy. In looking at the Paraho JP-5, a slight increase was seen in HC, CO, NOx as well as a slight decrease in fuel economy. The particulate was unchanged, as well as aldehydes and odor while phenols decreased somewhat with use of the

JP-5. The coal case resulted in a rather dramatic increase in HC, CO, NOx and particulate, on the order of approximately 50 percent. Fuel economy also increased, and phenols and odor went up slightly.

A solvent refined coal (SRC-2) fuel is currently being tested. While EPA has tested only Diesel fuels to date, EPA plans to test a Mobil MGT process gasoline (derived from methanol made from coal) and other gasolines as they are available. EPA will also test more Diesel fuels as they become available.

8. EPA has tested a heavy duty Volvo Diesel bus engine designed to run on methanol and Diesel fuel, each injected through its own injection system. The emission results from this engine were compared with those from a conventional Volvo Diesel engine using regular Diesel fuel. The use of the dual-fuel resulted in a 50% reduction in total particulate emissions compared to the single fueled engine. The particulate emitted from the engine using methanol had 70% organic extractables from the particulate, indicating far less elemental carbon type substances being formed compared to the conventional Diesel fueled engine, where about 30% organics were found. Less sulfate was also produced due to lower fuel sulfur levels. It was also found that the use of methanol decreased NOx by 56% for the 13 mode test and 35% for the transient cycle.

The use of methanol resulted in a hydrocarbon emissions increase, as measured by the heated FID, of about 40% for the 13 mode and 70% for the transient cycle compared to the Diesel fueled engine. Large quantities of unburned alcohol (which is only partially measured by the heated FID) were emitted. In one case, the amount of unburned methanol was four times the amount of hydrocarbons. Aldehyde emissions were also increased with the use of alcohol. The use of methanol resulted in a CO increase of about 60%. It was found that the use of an oxidation catalyst reduced both hydrocarbons and CO but some increase in NOx was found. The catalyst did not reduce particulate levels.

EPA is currently testing a Ford Escort with Anafuel (gasoline with a methanol based additive) and plans to test a VW designed to burn 100% methanol fuel.

9. EPA has also conducted work measuring nitrosamines (a potent carcinogen) in both Diesel crankcase emissions and vehicle interiors. Nitrosamines were found in Diesel crankcase emissions, possibly resulting from oil additives. Nitrosamines have also been found in vehicle interiors. Finally, nitrosamines may be present in Diesel exhaust, although this possibility is still unconfirmed. Preliminary data show that nitrosamine levels may be high ($1 \mu\text{g}/\text{m}^3$) along roadways and apparently these nitrosamines are mobile source related. It is not known if the Diesel crankcase and vehicle nitrosamines are entirely responsible for the roadside nitrosamine levels reported.
10. Various research projects, including some at EPA, have identified some of the compounds responsible for the Ames test activity of Diesel particulates. Apparently, polynuclear aromatic hydrocarbons themselves are responsible for only a small portion of the activity. However, various oxygenated polynuclear aromatic hydrocarbons (including hydroxy, ketone, carboxaldehyde, quinone, acid anhydride, and nitro compounds) have been identified in the "transition" fraction that accounts for significant Ames test activity.
11. EPA is currently developing a method to collect the gas phase HC in the exhaust for bioassay tests. A promising method being developed by ORD appears to be a cleaned-up XAD-2 resin. The hydrocarbons collected by this method may not have much Ames test activity compared with that of the particulate. However, OMSAPC has run some tests with a back-up filter containing treated Diesel particulates which shows that the HC collected does have Ames test activity that could be significant.
12. A number of Ames bioassay tests have been run on various samples collected by OMSAPC recently. Ames test work on the Diesel fuels project (discussed in Conclusion 6) showed that an increase in Ames test activity is associated with fuel aromatics. An increase in Ames test response was also seen when the cetane improver was used. Ames test work on samples collected from the dual fueled Volvo Diesel engine (discussed in Conclusion 8) indicated that the particulate from the dual fueled engine had lower Ames test activity than did the baseline engine

(i.e. pure Diesel fuel) over the transient cycle but higher activity over the 13 mode cycle. This apparent discrepancy may be explained by the fact that the dual-fueled engine showed much higher Ames test response for heavily versus lightly loaded modes. The 13 mode cycle is considered to be more heavily loaded than the transient cycle. There are also some data showing that the presence of a catalyst resulted in increased Ames test activity.

III. Recommendations for Future Work

The ECTD recommendations for future work are the following:

1. Synfuels. With the dramatic change in petroleum and fuel sources about to occur, it is extremely important that EPA remain abreast of the developments in this area. This is especially important with respect to the influence that these fuels may have on exhaust emissions products. There is currently a large level of effort on-going in the area of alternate fuel plant source emissions. However, very little work is currently planned on ultimate use or in-use emissions from the combustion of these fuels in vehicles. The fuels that should be tested in vehicles include coal liquids such as refined SRC-2, refined EDS and H coal liquids (made from direct coal liquefaction). The shale oil liquids should include those that may be available through the Union Oil process. Also it will be important to analyze different types of shale products, such as those made by in-situ retorts and other such methods. Other fuels that will be important to characterize include coal derived methanol, as well as actual methanol fuels (blends) from non-petroleum sources. Such alcohols should be looked at as well as alternative-source fuels. Also, gasolines should be tested, such as those from the Mobil MGT process as well as Naptha fractions, and others that are currently envisioned to be produced. By analyzing the emissions from these fuels, EPA will then be able to estimate the influence that they will have on ambient air quality.
2. New Technologies. As new technologies are developed it will be very important to remain abreast of the pollutants that may be emitted by them. Many technologies that have been introduced in the past have resulted in lower quantities of some pollutants. However, some of them have also resulted in increasing some pollutants that have been a concern. It is important to remain abreast of these new technologies so that if any pollutants are emitted that are hazardous to human health, an appropriate assessment of their impact can be made. New technologies might include the Ethyl lean burn system, various Diesel systems, such as the turbocompound and ceramic adiabatic engine or possibly various Diesel particulate trap technologies. New systems will be developed in the continued desire for improved fuel economy.

3. Bioassay. It will be very important to continue to analyze emissions from a variety of vehicles with bioassay techniques. For example, emissions from locomotives, possibly aircraft, motorcycles and other such sources that have never been analyzed should be given at least a preliminary bioassay characterization. Also, there is evidence showing that certain fuel additives appear to increase biological activity and this should be further investigated.

To date, ECTD has relied heavily on the Ames test to more or less routinely test Diesel particulates and other samples. While the Ames test has been a useful tool in comparing and investigating the bioactivity of various systems, the Ames test does have some limitations (e.g. it may not respond accurately to some nitrogen containing compounds). Future efforts should involve helping develop and use a simplified tier bioassay test system so that more accurate bioassay test data are obtained.

4. Malfunction conditions. Additional work should be done especially with Diesel engines under conditions outside of those normally recommended by the manufacturer. By analyzing emissions from vehicles under these conditions, a more realistic view of the pollutant burden emitted by such vehicles can be obtained.

This is especially important for heavy duty Diesel buses which operate in urban environments where the Diesel emissions can come in contact with large numbers of people. This is also important for light duty Diesels since very little work investigating their emissions under malfunction conditions has been done.

5. Gas phase analyses. EPA-ORD is currently completing the development of a gas phase sampling technique. ECTD should perform some testing with this technique to more adequately and fully characterize the gaseous emissions from a variety of different mobile sources. In this manner, EPA will be able to obtain a thorough estimate of the potential

impact of emissions from these mobile sources. This sampling should be performed on both light and heavy duty engines, including both gasoline and Diesel engines.

6. Specific pollutants. In the past, there has been some testing done on specific pollutants that are potentially very hazardous. Some additional work should be performed, for example, in the area of nitrosamines. Nitrosamines should be analyzed in Diesel exhaust where there is a tentative indication that they may be found. Also, there should be some additional nitrosamine monitoring along roadways to confirm the preliminary evidence of their existence there. Also in the past there have been specific compounds, such as dioxins, that had to be analyzed in a variety of exhaust sources. As these "pollutants of the month" arise, EPA should be in a position to respond in a rapid fashion and be able to analyze them.

IV. Characterization Results

A. Heavy Duty Diesels

1. Normal Operation

The more recent work with heavy duty Diesels has been done under EPA contract Number 68-03-2417, wherein a number of different engine variables were analyzed for their effect on engine pollutant emissions. The variables which were investigated included effects of 1) turbocharging, 2) exhaust gas recirculation (EGR), 3) changes in timing, 4) combustion system (direct or indirect injection), 5) fuel injection pressures, and 6) water injection. The data from this study of these six variables are presented in Table 1* and are discussed in the following paragraphs (1, 2 and 3).**

The engine which was used to determine the effects of turbocharging was a Daimler-Benz OM-352 and the turbocharged version, the Daimler-Benz OM-352A. Turbocharging, it is noted, decreased almost all of the pollutants for which analyses were made. The major exception to this was NO_x, which showed a slight increase. Aldehydes were almost unchanged, and the brake specific fuel consumption decreased.

The effects of timing were determined by testing a Caterpillar 3406 direct injection engine. By advancing the timing, increases were observed in HC, CO, NO_x, brake specific fuel consumption, sulfate and a very dramatic increase in aldehydes. The amount of particulate was reduced as well as the percent of extractable organics. By retarding the timing, a slight reduction in HC was observed, as well as a very slight increase in CO, a rather dramatic decrease in NO_x, and a slight increase in brake specific fuel consumption. The particulate rate increased rather markedly (i.e., by a factor of almost three), the percent of extractable organics also increased, as did the BaP emission rate and the sulfate emission rate. The odor level decreased; however, aldehydes increased by almost a factor of two.

* The data in this and other tables are usually based on single emission tests.

**Numbers in parentheses designate references given at the end of the paper.

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Table 1

Effect of Varying Engine Parameters on Pollutant Emissions - 13 Mode Cycle U

	Daimler-Benz		Caterpillar		Caterpillar 3406		Caterpillar		MACK ETAY(B) 673A		MACK ETAY(B) 673A	
	OH-352A		3406 DI		3406 DI		3406 DI		Standard		Standard	
	Naturally Aspirated	Turbo-charged	Standard Timing	Advanced Timing	52 Timing	102 Timing	DI - Std. Timing Without EGR	DI - Std. Timing With EGR	R. Bosch Pump(APE)*	APS R. Bosch Pump HI Pressure	Bosch Pump(APE)*	Standard APE Pump + 303 H ₂ O
HC, g/kW-hr	3.20	3.02	0.47	0.53	0.43	0.43	0.47	0.23	0.64	0.69	0.60	0.62
CO, g/kW-hr	7.00	4.08	3.13	5.63	3.16	3.16	3.13	6.43	2.13	1.68	1.64	1.75
NOx, g/kW-hr	9.98	11.95	13.09	18.53	7.02	7.02	13.09	7.35	8.87	12.06	8.52	6.59
MSFC, kg/kW-hr	0.294	0.284	0.253	0.262	0.273	0.273	0.253	0.268	0.243	0.234	0.240	0.239
Particulate, g/kW-hr	1.33	0.75	0.47	0.36	1.36	1.36	0.47	1.24	0.821	0.40	0.71	0.30
Organics, %	34.2	29.2	17.9	12.9	19.2	19.2	17.9	19.5	16.3	16.9	40.0	49.6
BaP, ug/kW-hr	1.43	1.17	0.20	1.26	0.69	0.69	0.20	0.11	0.23	0.08	0.18	0.22
Sulfate, mg/kW-hr	19.0	18.7	28.5	34.4	37.2	37.2	28.5	28.7	44.9	42.8	42.2	39.3
Odor, TIA	2.2	2.32	2.0	2.0	1.8	1.8	2.0	1.7	1.8	1.7	1.8	1.7
Aldehydes, mg/kW-hr	375.0	372.0	97.9	326.3	165.1	165.1	97.7	107.0	87.0	105.0	49.0	53.0

* These were 2 separate experimental runs using different APE pumps. Thus, the data are not necessarily the same.

The effect of EGR was tested with the Caterpillar 3406 direct injection engine with standard timing. By applying EGR, a slight increase in HC, a doubling of CO, a 50% reduction in NOx, a slight increase in brake specific fuel consumption and a 2.5 fold increase in particulate with associated increase in the percent of extractable organics were observed. The BaP went down almost by factor of two, the sulfates remained the same, there was a slight increase in odor and aldehydes were virtually unchanged.

The effect of direct and indirect injection were studied with the Caterpillar 3406 engine, which was tested in the direct injection mode and then changed to the indirect injection mode. With this change to indirect injection, a dramatic decrease was observed in HC, a decrease in CO, and again a decrease in NOx. Brake specific fuel consumption increased somewhat; however, the particulate rate decreased as well as the percent of extractable organics. The BaP rate also decreased but the sulfate rate increased somewhat. There was a rather marked decrease in odor; however, aldehydes were virtually unchanged.

The effect of the pump system was investigated with a Mack ETAY(B) 673A engine, wherein the engine was tested with a standard Robert Bosch fuel pump and then with a very high pressure pump. The results showed a slight increase in HC, a decrease in CO, a slight increase in NOx, and a slight decrease in brake specific fuel consumption. The most dramatic influence was the approximately 50% reduction in the particulate emission rate with almost no change in the percent of extractable organics. The BaP rate with the high pressure injection was 1/3 that obtained with the normal pump. Almost no change in sulfate, a slight decrease in odor, and a slight increase in aldehydes were seen.

The same Mack engine was used to analyze the effect of water injection on a variety of emissions. This testing involved the injection of approximately 30% water along with the fuel (DF-2) and here a slight increase was seen in HC and CO, a slight reduction in NOx, and brake specific fuel consumption

was almost unchanged. However, there was a very dramatic decrease in the particulate emission rate with an accompanying increase in the percent of extractable organics. The BaP rate also increased; however, it was noted that most of this increase was at idle conditions where presumably such an increase could be reduced by modulating water injection to eliminate water injection at idle speeds. The aldehyde emission rate was virtually unchanged.

Table 2 presents the percent organic extractables for particulate from four Diesel engines and one gasoline fueled engine burning leaded fuel. This showed a number of things including the trend towards much higher percent of organic extractables from the Diesel relative to the gasoline engine. It also showed that there was generally a dramatic decrease in the percent extractables as the load on the engine increased for the Diesel engines. The medium duty fleet of trucks is currently undergoing a rather marked conversion from gasoline to Diesel engines. In order to assess how such a conversion may influence regulated and unregulated emissions, a number of comparisons can be made between two engines of comparable applications in heavy duty trucks. These data are presented in Table 3 for two engines; one a Caterpillar 3208 which employed EGR and which was designed for California NOx standards, and a Chevrolet 366 CID gasoline-fueled engine designed for the same 1977 California standards. Here, much lower HC and CO emissions were generally seen with the Diesel engine along with slightly higher NOx emissions. Much lower brake specific fuel consumption was seen with the Diesel engine. However, the Diesel engine emitted over 12 times more particulate than the corresponding gasoline engine as well as a much higher percent of organics extractables. The BaP emissions, however, were somewhat lower from the Diesel engine than from the gasoline engine. Sulfate was much higher, due, of course, to the much higher level of sulfur in the Diesel fuel. The aldehydes from the Diesel engine were lower by a factor of approximately 10 compared to the gasoline engine.

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Table 2

Percent Organic Extractables
From Particulate For
Four Diesel And One Gasoline
Fueled Engines

<u>Condition Speed/Load(%)</u>	<u>MACK ETAY(B) 673A</u>	<u>Cater- pillar 3208 EGR</u>	<u>Cater- pillar 3406IDI</u>	<u>Daimler Benz OM- 352 N.A.</u>	<u>Chev- rolet 366</u>
Inter /02	34.8	17.0	12.9	37.3	2.4
Inter /50	9.3	6.7	4.5	57.2	4.0
Inter/100	3.5	2.7	5.1	7.1	2.0
Idle	15.5	8.2	9.9	17.1	6.1
Inter/CT*	NT@	23.3	NT	NT	5.6
High/100	1.0	2.7	0.8	7.4	3.9
High/50	6.3	2.2	11.7	51.6	2.6
High/02	38.5	9.4	35.9	59.1	1.7
High/CT*	NT	23.7	NT	NT	2.9

@ NT = Not tested
* close throttled

Table 3

Emissions From
Two Engines Used in Comparative
Application Vehicles - 23 Mode
Steady State Test

	Caterpillar 3208 with EGR - Diesel	Chevrolet 366 CID California (1977) Stds. Gasoline
HC, g/kW-hr	1.78	3.34
CO, g/kW-hr	8.51	73.76
NOx, g/kW-hr	5.07	4.56
BSFC, kg/kW-hr	0.290	0.463
Particulate, g/kW-hr	3.48	0.28
Organics, %	10.97	3.92
BaP, ug/kW-hr	2.31	3.02
Sulfate, mg/kW-hr	24.36	1.38
Odor, TIA	2.4	1-NA
Aldehydes, mg/kW-hr	109.0	1017.0

2. Malfunction Conditions

Almost all of the emissions data that are available from heavy duty engines have been gathered from engines that were tuned up to manufacturers' specifications. However, many of the engines that are operating on the roads today are not operating under a similar set of conditions, due to factors such as normal wear patterns, maintenance procedures, etc. Consequently our perception of their emissions could be dramatically different than may be the actual case.

In order to test this hypothesis, two engines were to be tested under EPA Contract No. 68-03-2706 with Southwest Research Institute (4). The first engine tested was a Cummins VTB-903 engine which is an engine normally used in bus applications. The engine was tested in its baseline condition (manufacturers' recommended specifications) and then altered to a malfunction condition. This malfunction condition was an increase in the fuel injector lash and a bleed-off of a certain portion of the turbocharger boost. Such a condition was one in which there would be virtually no noticeable decrease in power and therefore the operator would probably not bring in the vehicle for maintenance but would probably continue to operate it on the road. The data from this condition are presented in Table 4. When tested under this malfunction condition, increases in HC, CO, and a very slight decrease in NOx were seen along with an increase in the brake specific fuel consumption. The brake specific particulate also increased by a factor of approximately two, along with the organics, which went up by a factor of three on a g/km basis. Sulfates decreased somewhat, odor changed slightly, depending on whether the data were taken on the thirteen mode test or the transient cycle. Aldehydes increased by a factor of approximately five under the 13 mode test and stayed the same under the transient test. Phenols generally increased quite a bit under the 13 mode test condition but stayed almost the same or decreased somewhat under the transient test.

EPA is currently testing a Detroit Diesel 6V-71 N engine under a set of malfunction conditions that are similar to those of the Cummins in that they are severe enough to alter the emissions yet not severe enough that the operator would return the vehicle to the shop for maintenance. These data

Table 4

Emissions Results from
A 4-Stroke Cycle Heavy Duty
Engine (Cummins VTB-903)
Operated Under Baseline And
Malfunction Conditions

	13 Mode		Transient	
	<u>Baseline/Malfunction</u>		<u>Baseline/Malfunction</u>	
HC, g/kW-hr	0.96	3.94	1.79	6.98
CO, g/kW-hr	2.20	3.55	1.87	3.12
NOx, g/kW-hr	9.29	9.25	7.83	7.63
BSFC, kg/kW-hr	0.254	0.269	0.269	0.288
Particulate, g/kW-hr	0.32	0.57	0.50	1.08
Organics, %	38.4	55.4	51.2	76.9
Organics, g/kW-hr	0.123	0.316	0.256	0.829
Sulfate, mg/kW-hr	39.5	33.3	38.4	33.4
Odor, TIA	1.58	1.74	1.17	1.32
Aldehydes, mg/kW-hr	33.4	108.12	101.0	99.0
Phenols, mg/kW-hr	5.7	66.0	15.4	10.2

will be available within the next several months. Malfunction data of this type are very important as they give a realistic view of how these engines operate under actual conditions. Additional work should be done on heavy duty engines but an more extensive effort should be performed with light duty Diesel engines for which no data of this type are available.

B. Light Duty Diesels

Table 5 presents data from the work performed under EPA contract 68-03-2414 wherein the emissions from what were, at the time of testing, prototype Diesels were compared against their gasoline counterparts (5 and 6). This work showed that the hydrocarbon emissions were generally higher from the Diesel than the gasoline fueled vehicles. However, CO was lower as well as oxides of nitrogen. The fuel economy for the Diesel engine was, of course, much better from the Diesel than the gasoline fueled engine. The Diesel engine also had a much higher particulate rate as well as an organic emissions rate. The BaP and sulfate emission rates from the Diesel engine were much higher than those from the gasoline engine. Aldehydes from the Oldsmobile vehicles were much higher with the Diesel than the gasoline engine; however, aldehydes were almost equal from the Volkswagen Diesel and gasoline vehicles.

Continued work should be done on a spot monitoring basis to evaluate the emissions from light duty Diesel engines.

C. Light Duty Gasoline Vehicles

Much of the testing of light duty gasoline vehicles has been performed when the vehicles have been tuned to manufacturers' specifications. However, many vehicles operate in a condition that is outside those specified by the manufacturer. In order to estimate the levels of pollutants that are emitted by vehicles under such operating conditions, EPA conducted a thorough program (7, 8, 9, 10, 11, 12 13) to test a number of vehicles operated under several malfunction conditions. These conditions included rich-best-idle, 12% misfire, disabled exhaust gas recirculation, higher oil consumption (obtained by oil injection), and rich-best-idle with no air injection.

Table 5

Emissions Results From
Comparative Diesel and Gasoline
Fueled Vehicles - FTP Cycle

	<u>Oldsmobile Cutlass</u>		<u>Volkswagen Rabbit</u>	
	<u>Diesel</u>	<u>Gasoline</u>	<u>Diesel</u>	<u>Gasoline</u>
Displacement in ³	350**	260**	89.7	97.1
HC, g/km	0.47	0.24	0.23	0.14
CO, g/km	1.24	1.34	0.49	2.30
NOx, g/km	0.70	0.85	0.54	0.63
Fuel Economy, mpg	21.7	15.6	42.7	24.6
Particulate, g/km	0.57	0.006	0.18	0.004
Organics, %	13.3	10.7@	21.4	42.3*
BaP, ug/km	4.54	0.17@*	2.67	0.17@*
Sulfate, mg/km	9.96	1.37	3.66	0.04
Odor, TIA	1.2	N.T.@@	1.1	N.T.
Aldehydes, mg/km	80.7	14.0	39.6	35.1

@ = FET cycle

* = Hot FTP cycle

@* = BaP values are considered conservative and should be used with caution due to inadequacies of sampling method.

@@ = NT=not tested

** = These engines were selected to have equal performance (e.g. equivalent vehicle acceleration) rather than equal displacement.

The data from four oxidation catalyst equipped vehicles and one baseline non-catalyst equipped vehicle are presented in Table 6 which gives the number of vehicles that experienced emissions increases during malfunction relative to the baseline state. Most of the malfunctions resulted in an increase in hydrocarbon emissions as well as carbon monoxide. The misfire and disabled EGR conditions resulted in increases in oxides of nitrogen, whereas the remainder of the malfunctions did not have any influence on NOx. Most of the malfunctions resulted in increases in most of the other emission (e.g. unregulated) with a few minor exceptions.

In trying to estimate the importance of these data, the maximum emission rate (MER) that was experienced by any of the vehicles tested under any of the conditions tested was related to the threshold limit value (TLV) as given in Table 7. The threshold limit values are those established by OSHA for exposure in an eight-hour work shift. For the compounds listed it would appear that the higher the MER to TLV ratio the more likely the maximum emission rate would be a source of concern. However, it should be emphasized that definite conclusions are currently inappropriate for any of the compounds studied with a possible exception of those for which automotive emissions standards have been established. EPA is currently looking at various unregulated emissions and plans to define an acceptable level from many of these unregulated emissions to the extent possible. It should also be observed that some of the compounds which are considered by OSHA and other agencies as being non-toxic can have a potential indirect harmful effect. An example of this would be nitrous oxide, due to its potential negative effect on the upper atmospheric ozone layer. In reviewing Tables 6 and 7 it is observed that the maximum FTP composite emission rates for HC and NOx greatly exceeded the standards for 1983. The maximum value for total particulates, however, was less than one-half of the proposed 0.2 gpm particulate standard for 1983 Diesel vehicles which would be expected since gasoline vehicles using unleaded fuel typically have very low particulate emissions. The maximum undiluted exhaust emission rates for carbon monoxide and oxides of nitrogen exceed the TLV by over 100. Other compounds in the undiluted exhaust which exceed an established TLV include benzene and

Table 6

Number of Cars with Emissions Increase During Malfunction*
-Baseline (non-catalyst) and Oxidation Catalyst Equipped Vehicles-

	Number of Cars for Which Emissions Increased/ The Total Cars Evaluated in that Configuration				
	Rich Best Idle	12% Misfire	Disabled EGR	High Oil Consump.	R.B.I. and No Air Inj.
<u>Regulated Emissions</u>					
Hydrocarbons	4/5	5/5	a	3/3	2/2
Carbon Monoxide	5/5	5/5	a	3/3	2/2
Oxides of Nitrogen	0/5	5/5	5/5	0/3	0/2
<u>Particulates</u>					
Total Particulates	2/4	4/5	3/5	3/3	2/2
Sulfate	1/5	2/5	0/5	3/3	1/2
<u>Compound Group Totals</u>					
Aldehydes & Ketones	4/5	5/5	5/5	1/3	1/2
Individuals Hydrocarbons **	4/4	2/2	1/2	---	---
Organic Sulfides	2/3	2/4	0/3	1/3	1/2
Organic Amines ^b	5/5	1/4	2/5	1/3	1/2
<u>Other Compounds</u>					
Ammonia	3/5	3/5	2/5	---	1/1
Cyanide & Cyanogen	4/5	3/5	5/5	---	1/1
DMNA ^c	---	---	---	---	---
Hydrogen Sulfide	4/5	1/5	1/5	1/3	2/2
Nickel Carbonyl ^d	---	---	---	---	---
Nitrous Oxide	2/5	2/3	3/3	0/1	1/2
<u>Other Elements^c</u>					

^a Changes were relatively minor and inconsistent

^b Changes in organic amines were relatively minor

^c Discussed separately

^d No nickel carbonyl was ever detected

* Vehicles were:

Year	Make and Model	Engine CID/CYL	Emission Controls	
			Oxidation Catalyst	Air Pump
1977	AMC Pacer	258/6	None	Yes
1978	Chev. Malibu	305/8	Pelleted	No
1978	Chev. Malibu (Cal.)	305/8	Pelleted	Yes
1978	Ford Granda	302/8	Monolith	Yes
1978	Ford Mustang II	302/8	Monolith	No

**Individual HC consist of lower molecular weight hydrocarbons (methane, ethane, ethylene, acetylene, propane, propylene, benzene, and toluene) measured by gas chromatography.

Table 7

Relative Importance of Malfunction Emission Rates
Baseline (non-catalyst) and Oxidation Catalyst Equipped Vehicles

	Maximum Emission Rate (MER) in mg/km ^a	Emission Standard for 1983 in mg/km	Equivalent MER in Undiluted Exhaust in mg/m ³ (MEC)	Threshold Limit Value (TLV) in mg/m ³ OSHA	R ^e	Ratio of MEC to TLV
<u>Regulated Emissions</u>						
Hydrocarbons	10800 ^b	255	7000	--	--	--
Carbon Monoxide	52900	2113	34400	55	--	625
Oxides of Nitrogen	4200	622 ^c	2700	9	--	300
<u>Particulates</u>						
Total Particulates	48 ^b	124 ^d	31	--	1	31 ^e (12) ^f
Sulfates	17	--	15	--	1	15 ^e
<u>Compound Group Totals</u>						
Aldehydes & Ketones	228 ^b	--	228	--	--	--
Organic Sulfides	2	--	2	--	10	<1 ^e
Organic Amines	<1	--	<1	--	>10	<1 ^e
<u>Other Compounds</u>						
Ammonia	57	--	37	35	--	1
Cyanide & Cyanogen	7 ^b	--	7	--	5	1 ^e
Hydrogen Sulfide	4	--	4	--	10	<1 ^e
Nickel Carbonyl	0.00	--	0.00	0.007	--	0
Nitrous Oxide	70	--	60	--	--	--
Formaldehyde	151 ^b	--	151	4	--	38(2) ^f
Benzene	230 ^b	--	182	33	--	5

^a FTP rate recorded for the regulated emissions

^b Value for non-catalyst car - Highest HC value for catalyst car was 2300

^c 255 mg/km in California

^d Proposed for diesel cars

^e Based on values for some similar or Related compounds as set by OSHA(9)
or Recommended by the 1968 American Conference of Governmental Industrial
Hygienists(10)

^f Value for catalyst cars given within the parentheses if the value for
non-catalyst and catalyst equipped vehicles differs substantially

formaldehyde. Even though benzene and formaldehyde are both suspected carcinogens, they also are toxic and the TLVs are based on their toxicity. (The maximum value for ammonia was approximately equal to the TLV). As a matter of possible interest, the value for carbon dioxide was over 20 times the established TLV. For the remaining compounds and compound groups, it was necessary to estimate an equivalent TLV based on best available data. Based on these estimated values, the maximum levels for total particulates and sulfate were above the estimated values for an equivalent TLV.

Emissions from a total of four 3-way and 3-way plus oxidation catalyst vehicles have also been analyzed and the resultant data are presented in Tables 8 and 9. The same general trend is apparent with these vehicles as with the oxidation catalyst vehicles, wherein the emissions of a variety of compounds tend to increase with the malfunction conditions. The same type of analysis was made with regards to the maximum emission rate compared to the OSHA eight-hour TLV. It is observed that the maximum undiluted exhaust emission concentrations for carbon monoxide and oxides of nitrogen exceeded the TLV by more than the factor of 100. Other compounds for which the maximum emission rate exceeded an established TLV included benzene and ammonia. (The maximum values for organic sulfides, hydrogen sulfide, and formaldehyde were almost equal to the TLV). As a matter of possible interest, the value for carbon dioxide was again over 20 times the established TLV. For the remainder of the compounds it was necessary to estimate an equivalent TLV based on best available data. Based on these estimated values, the maximum levels for total particulate, sulfates, and cyanide and cyanogen were above the estimated values for an equivalent TLV.

It appears as though the following general comparisons may be made for this malfunction work. Sulfate, ammonia, and nitrous oxides were higher from catalyst equipped cars than from the one non-catalyst car. Hydrocarbons and aldehydes were highest from the non-catalyst car. Ammonia and cyanides were highest from the three-way catalyst cars. It appears that the unregulated exhaust emissions composition from catalyst equipped cars operating under malfunctioning conditions is in general distinguishably different from that of non-catalyst cars.

Table 8 - Selected FTP Regulated and Unregulated Emissions
From 3-Way Catalyst Equipped Gasoline Fueled Vehicles

	Emissions, mg/km				
	Unmodified	Disabled Oxygen Sensor	12K Misfire ^a	Disabled ECR ^b	High Oil Cons.
Car 41, Pinto (3-Way + Oxid./Air)					
Hydrocarbons	0.1	0.1	0.4	0.1	--
Carbon Monoxide	1.3	1.9	2.4	1.8	--
Oxides of Nitrogen	0.5	0.3	0.3	0.7	--
Fuel Consumption	11.1	12.0	11.2	11.8	--
Total Particulates	15.3	2.9	6.5	19.7	--
Sulfates	3.13	1.03	0.80	12.25	--
Ammonia	6.0	10.2	6.53	13.2	--
Cyanide & Cyanogen	0.1	--	0.1	0.0	--
Car 42, Sunbird (3-way only)					
Hydrocarbons	0.2	1.5*	1.1*	1.4*	--
Carbon Monoxide	2.6	57.5*	4.7	47.6*	0.2
Oxides of Nitrogen	0.5	0.1	0.4	0.2	3.0
Fuel Consumption ^{***}	10.9	12.7**	10.9	12.2**	0.6
Total Particulates	5.6	11.1	7.5	28.7	11.3
Sulfates	0.21	0.32	0.16	0.12	6.0
Ammonia	11.1	68.1	36.7	93.9	0.20
Cyanide & Cyanogen	1.01	4.13	4.09	6.97	5.31
Car 42, Saab 99 (3-way only)					
Hydrocarbons	0.1	0.7*	2.2*	--	--
Carbon Monoxide	2.1	20.0*	11.1*	--	0.1
Oxides of Nitrogen	0.1	0.2	0.1	--	2.3
Fuel Consumption	10.8	11.6	13.0**	--	0.1
Total Particulates	4.9	8.9	17.1	--	11.8
Sulfates	0.19	0.40	0.31	--	6.4
Ammonia	60.8	400.5	142.5	--	0.14
Cyanide & Cyanogen	1.1	66.9	7.5	--	63.3
Car 51, Marquis (3 way + Oxid./Air)					
Hydrocarbons	0.1	0.1	1.7*	1.5*	--
Carbon Monoxide	1.6	1.0	8.9*	36.5*	--
Oxides of Nitrogen	0.8	2.5*	0.6	0.6	--
Fuel Consumption	15.8	15.5	16.4	17.1	--
Total Particulates	2.0	5.8	10.0	5.8	--
Sulfates	0.85	1.30	0.13	0.17	--
Ammonia	5.1	3.4	30.9	172.4	0.21
Cyanide & Cyanogen	0.31	0.13	1.57	69.96	253.0
					112.29

^aWith air to bypass for Car 51.

^bOxygen sensor disabled with Cars 41 and 42 and air to bypass with Car 51.

^cDisabled oxygen sensor and air pump with Car 41, disabled oxygen sensor and rich-
best-idle with Car 43, and disabled cold temperature sensor with Car 51.

^dValues exceeding 1978 California standards (0.25, 5.6, 0.9 for HC, CO, NOx).

^eGreater than ten percent increase in fuel consumption relative to unmodified.

^{***}Liters / 100km

Table 9

Relative Importance of Maximum Emission Rates
From 3-way Catalyst Equipped Vehicles

	Maximum Emission Rate (MER) in mg/km	Emission Standard for 1983 in mg/km	Equivalent MER in Undiluted Exhaust in mg/m ³ (MEC)	Threshold Limit Value (TLV) in mg/m ³ OSHA (8) R ^c		Ratio of MEC to TLV
<u>Regulated Emissions</u>						
Hydrocarbons	1,800 ^a	255	1,100	--	--	--
Carbon Monoxide	52,400 ^a	2,113 ^b	31,400	55	--	571
Oxides of Nitrogen	2,500 ^a	622 ^b	1,500	9	--	167
<u>Particulates</u>						
Total Particulates	11 ^a	124 ^d	7 ^e	--	1	7 ^e
Sulfate	27	--	24	--	1	24
<u>Compound Group Totals</u>						
Aldehydes & Ketones	3	--	2	--	--	--
Organic Sulfides	1	--	1	--	10	<1
Organic Amines	<1	--	<1	--	>10	<1
<u>Other Compounds</u>						
Ammonia	253	--	152	35	--	4
Cyanide & Cyanogen	112	--	67	--	5	13
Hydrogen Sulfide	3	--	3	--	10	<1
Nickel Carbonyl	0	--	0	0.007	--	0
Nitrous Oxide	88	--	53	--	--	--
Formaldehyde	2	--	2	4	--	<1
Benzene	125	--	75	33	--	2

^a FTP rate recorded for the regulated emissions and total particulates

^b 255 mg/km in California

^c Based on values for some similar or Related compounds as set by OSHA (8)
or Recommended by the 1968 American Conference of Governmental Industrial
Hygienists (9)

^d Proposed for Diesel cars

^e Values were 44 for the HFET

D. Fuels

1. Fuels Variables

Under EPA contract 68-03-2440 with Southwest Research Institute, the emissions from two different light duty Diesel vehicles (Mercedes Benz 240D and Volkswagen Rabbit) were tested as a function of five different fuels that were blended for use in this program (5 and 14). These fuels were 1) the Emissions Test Fuel that has been used by EPA for Diesel testing since the late 1960's, 2) a fuel that has the properties of the "national average" Diesel Fuel, 3) Diesel Fuel number 1, 4) a minimum quality fuel more typical of the direction towards which today's Diesel fuels are headed, and 5) a premium quality fuel. The data from this testing are presented in Tables 10 and 11. When the vehicles were tested with those fuels, little change was seen in hydrocarbon emissions with the exception of the minimum quality fuel, which increased the HC emission rate. The same was true of carbon monoxide emissions. The Volkswagen was generally insensitive to fuels variables with regards to NOx emissions; however, the NOx emissions went up in the Mercedes with the use of the minimum quality and the premium quality fuel. Fuel economy generally decreased with the minimum quality and the premium quality fuels. The most marked change came with particulate with the minimum quality fuel resulting in a much higher particulate rate in both vehicles. The percent extractables also was higher. These results, when combined together, showed a much higher organics emissions rate for the minimum quality fuel in the Volkswagen; however, in the Mercedes Benz virtually no change in the organics emissions rates in terms of g/km was seen as a function of the five fuels. BaP was generally unaffected by four of the fuels; however, the minimum quality fuel showed a marked increase in the BaP emission rate. With aldehydes, a marked increase occurred with the minimum quality fuel.

This work was followed by EPA contract 68-03-2707 wherein the very specific fuel properties were varied with a base fuel to note their effect on emis-

Table 10

Emissions Results
From a Volkswagen Rabbit Diesel
Operated on Five Different Fuels
- FTP Cycle -

	2D Emissions Test Fuel	2D National Average	1D "Jet A"	2D Minimum Quality	2D Premium Quality
HC, g/km	0.18	0.20	0.17	0.71	0.20
CO, g/km	0.49	0.51	0.55	0.81	0.52
NOx, g/km	0.59	0.65	0.57	0.58	0.63
Fuel Economy, mi/gal	41.2	42.0	41.2	38.1	39.9
Particulate, g/km	0.225	0.218	0.177	0.375	0.194
Organics, %	10.8	13.2	15.0	15.6	13.6
Organics, g/km	0.024	0.029	0.027	0.059	0.026
BaP, ug/km	1.13	1.33	1.18	3.64	1.05
Aldehydes, mg/km	28.7	12.6	18.0	52.5	13.4

Table 11

Emissions Results
From a Mercedes Benz 240D Diesel
Operated on Five Different Fuels
- FTP Cycle -

	2D Emissions Test Fuel	2D National Average	1D "Jet A"	2D Minimum Quality	2D Premium Quality
HC, g/km	0.12	0.19	0.09	0.20	0.12
CO, g/km	0.57	0.64	0.57	0.71	0.68
NOx, g/km	0.78	0.79	0.73	0.88	0.85
Fuel economy, mi/gal	27.7	27.3	27.6	25.1	25.1
Particulate, g/km	0.329	0.314	0.235	0.380	0.292
Organics, %	11.2	9.8	12.0	7.6	8.9
Organics, g/km	0.037	0.031	0.028	0.029	0.026
BaP, ug/km	0.39	0.46	0.32	0.62	0.23
Aldehydes, mg/km	16.9	15.9	16	23.9	16.9

sions (15). The test vehicle was a Mercedes Benz 240D. The data are presented in Table 12. The principal results that were observed from this work are the following.

1. Regulated gaseous emissions were not strongly affected by the fuel variables studied. Hydrocarbon and CO emissions increased slightly with the high aromatic and cetane-improved aromatic blends. The cetane-improved aromatic blend also resulted in a small NO_x increase. The cetane improver (DII-3) is an alkyl nitrate compound made by Ethyl Corporation.
2. Aldehyde emissions were largely unaffected by fuel changes, with the exception of a fuel designated EM-405-F (base fuel + isoquinoline at 0.1% N). The increase in aldehydes was substantial, but not completely understood. The light-end and heavy-end blends also resulted in slight aldehyde increases, but not of the magnitude observed with EM-405-F.
3. Phenol emissions (which are co-carcinogenic) were strongly affected by the shale oil blend. They increased to over 60 times the level observed with base fuel. The only other pronounced increase in phenols occurred while testing EM-405-F, base + isoquinoline (0.1% N).
4. Particulate rates were reduced with the light-end blend and the olefin blend, by 14 percent and 6 percent, respectively. The two blends containing aromatics were associated with increases in particulate emissions of about 27 percent. The cetane-improved aromatic fuel blend increased particulate emissions about 68 percent over those observed with base fuel. Heavy ends fuel apparently did not cause an increase in particulate emissions, as might have been expected.
5. Blends containing aromatics resulted in slightly less organic solubles extracted from particulate matter. Olefins, light ends, and heavy ends were associated with increases in the amount of organic solubles.

Table 12

Emissions Results From
A Mercedes 240D Diesel Vehicle Operated
on a Variety of Fuels - FTP Cycle

	Base Fuel (H 320)	Base + isoquinoline 0.05 % N	Base + isoquinoline 0.12 % N	Base + Shale Oil Cut 0.052 % N	Base + 31% Exxon "HAN" heavy aromatics	Base + 6% Chevron alpha olefins	Base + light ends	Base + 30% Pure aromatics	Base + heavy ends	Base + 31% "HAN" + 0.7% DII-3
HC, g/km	0.09	0.08	0.08	0.09	0.12	0.09	0.11	0.13	0.08	0.13
CO, g/km	0.52	0.47	0.46	0.52	0.59	0.48	0.48	0.60	0.47	0.66
NOx, g/km	0.75	0.76	0.89	0.87	0.88	0.85	0.82	0.92	0.86	1.04
Fuel Economy, ml/gal	24.9	24.8	24.5	24.1	24.7	23.9	24.7	24.6	24.4	24.4
Particulate, mg/km	165	162	162	180	212	155	142	219	159	287
Organics, %	18.4	16.0	16.0	12.7	11.8	13.9	19.9	11.7	17.5	10.8
Organics, mg/km	30.4	25.9	25.9	22.9	25.0	21.5	28.3	25.6	27.8	31.0
BaP, ug/km	0.53	0.26	0.35	0.96	0.37	0.21	0.51	0.73	0.43	0.43
Odor, TIA	0	0	0.98	0	1.31	1.45	1.35	0.89	1.09	1.05
Aldehydes, mg/km	0.61	0.31	15.22	0.00	2.79	0.00	8.18	0.00	8.83	0.00
Phenols, mg/km	1.34	4.33	29.40	127.96	0.66	0.14	0.21	1.30	0.55	0.18

6. BaP emissions were generally low for the fuel blends tested, ranging from 0.25 to 0.96 ug/km. A slight reduction was associated with the olefin blend. A significant increase in BaP, 3 times, was exhibited by the shale oil blend EM-430-F when compared to the base fuel.

2. Alternate Fuels

a. Middle Distillates Derived from Alternate Sources

Under the current task order contract (EPA Contract No. 68-03-2884) with Southwest Research Institute, some alternate fuels evaluations are being conducted with a Volkswagen Rabbit Diesel (15). So far, four fuels have been tested which include a base Diesel fuel #2, a Diesel fuel marine #2 obtained from shale oil, a Paraho JP-5 as well as a Coal Case 5A. These fuels are described in Table 13. The emissions from these fuels are presented in Table 14. Here it was seen that there was virtually no change in HC, CO and NOx emissions with the shale marine fuel. This was also true of the particulate emission rate. The aldehydes, however, decreased slightly. The phenols stayed much the same, as well as the odor. There was a slight decrease in the fuel economy. In looking at the Paraho JP-5, a slight increase was seen in HC, CO, and NOx as well as a slight decrease in fuel economy. The particulate was unchanged, as well as aldehydes and odor while phenols decreased somewhat with use of the JP-5. The coal case resulted in a rather dramatic increase in HC, CO, NOx and particulate (on the order of approximately 50 percent), fuel economy also increased, and phenols and odor went up slightly.

A combination blend of 35% Solvent Refined Coal 2 (SRC2) has been tested, which resulted in smoke levels that were very very high during the first 105 seconds of the LA4. The smoke and particulate levels were so high that the sampling system failed and thus testing was unable to be continued. The SRC2 will be blended at a lower level (approximately 25%) in an attempt to have the engine operate without exceeding the limits of the sampling system. Other fuels such as an Exxon EDS fuel and a naptha cut will be tested in the near future. Other such fuels will also be tested as they become available (16).

TABLE 13 FUEL PROPERTIES AND COMPOSITION

Substance	Base DF-2	Shale Diesel Marine	Paraho JP-5	Coal Case 5A	SRC-II Med. Cetane	Broadcut Mid-Continent
Fuel Code (EM-)	329-F	453-F	473-F	474-F	475-F	476-F
Cetane No. (D613)	50	49	45	42		35
Cetane Index (D976)	52	56	46	41		57
Gravity, °API @ 60°F	37.5	37.9	43.6	31.1		44.1
Density, g/ml @ 60°F	0.837	0.835	0.808	0.870		0.806
Carbon, wt. %	85.8	86.3	85.9	86.5		86.1
Hydrogen, wt. %	13.0	13.4	13.7	12.4		13.2
Nitrogen, ppm (oxid. pyrolysis)	48	5	<1			
Sulfur (lamp), %	0.24	<0.005	<0.005	0.10		0.17
Calculated H/C, numeric	1.81	1.85	1.90	1.71		1.83
Carbon No. range (G.C.)	8-24	9-20				
Aromatics, vol. %	21.3	28.5	22.	34.9		16.2
Olefins, vol. % (D1319)	1.7	2.1	2.	1.4		0.0
Paraffins, vol. %	77.0	69.4	76.	63.7		83.8
Viscosity, cs @100 °F (D445)	2.36	2.61	1.38	3.08		1.53
Gum, mg/100 ml (D481)	14.3	0.3	0.0	42.4		
Total solids, mg/l.	7.4	0.3				
Metals in fuel, x-ray	0a	0a				
Boiling Range, °C (IBP-EP, D86)	191-340	207-317	179-248	192-366		21-354
10% point	219	236	189	234		93
20% point	231	246	192	244		137
30% point	242	252	196	253		159
40% point	251	259	198	259		197
50% point	260	266	202	267		230
60% point	269	272	206	276		250
70% point	278	278	211	277		262
80% point	290	286	218	292		282
90% point	307	295	228	330		327
95% point	323	302	237	353		-
Residue, wt. % (D86)	1.3	1.0	1.5	1.5		1.0

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TABLE 13 (Cont'd). FUEL PROPERTIES AND COMPOSITION

Substance	Base DF-2	Shale Diesel Marine	Paraho JP-5	Coal Case 5A	SRC-II Med. Cetane	Broadcut Mid-Continent
Fuel Code (EM-	323-F	453-F	473-F	474-F	475-F	476-F
Boiling Range, °C (IBP-EP, D2887)	104-387	118-341				
10% point	197	216				
20% point	220	237				
30% point	239	254				
40% point	256	265				
50% point	268	274				
60% point	280	285				
70% point	292	297				
80% point	307	307				
90% point	330	319				
95% point	347	325				
Residue, wt. % (D2887)	0.0	0.0				
Composition, Volume %						
Kerosene						
Petroleum	0.0	0.0	0.0	17.3	0.0	22.0
JP-5	0.0	0.0	100.0	0.0	0.0	0.0
JP-8	0.0	0.0	0.0	0.0	0.0	0.0
Diesel						
Petroleum	100.0	0.0	0.0	66.7	65.0	23.0
Shale DFM	0.0	100.0	0.0	0.0	0.0	0.0
Coal SRC-II	0.0	0.0	0.0	16.0	35.0	6.2
Light Cycle Oil	0.0	0.0	0.0	0.0	0.0	5.2
LSR Naptha	0.0	0.0	0.0	0.0	0.0	7.4
HSR Petroleum	0.0	0.0	0.0	0.0	0.0	4.8
Shale	0.0	0.0	0.0	0.0	0.0	20.9
Coal (Simulated)	0.0	0.0	0.0	0.0	0.0	0.0
N-Butane	0.0	0.0	0.0	0.0	0.0	10.5

^a<10 ppm of Cr, Fe, Ni, Cu, Zn, and Mg; <70 ppm Pb; <100 ppm Al and Si

Table 14
Emissions
From Volkswagen Rabbit
Diesel Operated on a Baseline
DF2 Diesel Fuel and Three "Synthetic" Fuels

Emissions	Fuel → Base DF-2	Shale Diesel Marine #2	Paraho JP-5	Coal Case 5A
HC, g/km	0.31	0.31	0.38	0.39
CO, g/km	0.96	1.06	1.20	1.21
NOx, g/km	0.66	0.67	0.70	0.83
Fuel Economy, mi/gal	36.9	35.5	35.5	37.8
Particulate, g/km	0.25	0.27	0.25	0.32
Aldehydes, mg/km	14.0	9.0	13.0	N.Y.A.*
Phenols, mg/km	12.0	11.0	0.5	14.0
Odor, TIA	2.3	2.2	2.4	2.8

* N.Y.A. = not yet available

b. Gasolines Derived from Alternate Sources

In the near future, EPA will be testing a gasoline made from methanol via the Mobil MGT process and also a gasoline that was blended to specifications. This latter fuel was blended by the Army Fuels and Lubricants Laboratory at Southwest Research Institute and will have properties similar to a synthetic gasoline from oil shale. Also future possibilities include the SASOL/Kentucky coal run that is currently underway, which should produce some gasoline that may become available for EPA tests. Also, Union Oil Company is currently under contract to DOE to produce some gasoline from oil shale which may be tested by EPA. These last two sources of alternate gasolines are very tentative and would only be seen in the somewhat distant future. Efforts continue to obtain these samples for ECTD testing (16).

To date, ECTD has performed no characterization on alternate source gasolines due to their lack of availability. In spite of the fact that EPA had a contract since 1976 with Southwest Research Institute to do gasoline synthetic fuel work, EPA has been unable to obtain synthetic gasoline samples (17). Efforts were made to obtain some from the SASOL plant in South Africa, but they were unwilling in the end to provide fuel samples to EPA.

c. Alcohol Fuels

Some testing and characterization has been performed by ECTD/CTAB on vehicles fueled with alcohols with more such testing planned for the near future. One major project that has just been completed involved the testing of an alcohol-fuel/Diesel-pilot compression-ignition engine from Volvo, as well as its heavy duty Diesel counterpart (18, 19). The dual-fueled engine uses Diesel fuel for pilot injection, which initiates combustion and then uses a variable amount of alcohol, injected subsequent to the pilot injection for the principal combustion. This engine was tested with both methanol and ethanol plus water, as well as a limited number of tests with an oxidation catalyst added to the dual fueled engine. The counterpart engine, fueled exclusively with Diesel fuel, was also tested.

The results from this work are presented in Table 15. It was found that the use of methanol resulted in a 50% reduction in total particulate emissions compared to the single fueled engine. The particulate emitted from the engine using methanol had 70% organic extractables from the particulate, indicating far less elemental carbon type substances being formed as was the case with the conventional Diesel fueled engine, where about 30% organics were found. Less sulfate is also produced due to lower fuel sulfur levels. It was also found that the use of methanol decreased NOx by 56% for the 13 mode test and 35% for the transient cycle.

The use of methanol resulted in a hydrocarbon emissions increase, as measured by the heated FID, of about 40% for the 13 mode and 70% for the transient cycle compared to the Diesel fueled engine. Large quantities of unburned alcohol (which is only partially measured by the heated FID) were emitted. In one case, the amount of unburned methanol was four times the amount of hydrocarbons. Aldehyde emissions were also increased with the use of alcohol. The use of methanol resulted in a CO increase of about 60%. It was found that the use of an oxidation catalyst reduced both hydrocarbons and CO but some increase in NOx was found. The catalyst did not reduce particulate levels. Ames test data were accumulated on these fuels and will be presented in the Ames test data section.

Testing has also been performed on a Ford Escort fueled by gasoline as well as a blend of Anafuel, which is an alcohol-based additive blended with gasoline (15). The preliminary results from this work, based on limited testing, showed a slight decrease in exhaust HC, approximately a 70% decrease in CO, a 25% increase in NOx, no change in fuel economy, and a decrease in particulate when the Anafuel case was compared to the gasoline case. No ethanol or methanol was emitted from the engine when either fuel was used. With the base fuel, there were negligible quantities of aldehydes emitted and when the Anafuel was used, there was a very slight increase in this level of aldehyde. The vehicle appeared to run well on both fuels. Again, the results with the Anafuel are preliminary and may not be confirmed with further testing. Some additional EPA in-house testing showed similar results and also a large increase in evaporative HC emissions.

TABLE 13. SUMMARY OF COMPOSITE EMISSION RATES FROM THE VOLVO TD-100C DIESEL ENGINE AND THE VOLVO TD-100A DIESEL/ALCOHOL ENGINE

Composite Emission Rates	Engine Test Configuration									
	Diesel Volvo TD-100C		Methanol Volvo TD-100A		Methanol-Catalyst Volvo TD-100A		Ethanol Volvo TD-100A		Ethanol-Catalyst Volvo TD-100A	
	13-mode	Transient	13-mode	Transient	13-mode ^a	Transient	13-mode	Transient	13-mode	Transient
Federal Test Procedure (FTP)										
Hydrocarbon, HC _b g/kw-hr, (g/lp-hr)	1.05 (0.78)	1.15 (0.85)	1.45 (1.08)	1.95 (1.45)	0.16 (0.12)	0.22 (0.16)	1.65 (1.23)	2.27 (1.69)	0.60 (0.45)	0.63 (0.47)
Carbon Monoxide, CO g/kw-hr, (g/lp-hr)	3.18 (2.37)	4.04 (3.01)	9.55 (7.12)	10.29 (7.67)	0.83 (0.62)	3.74 (2.79)	10.53 (7.85)	12.89 (9.61)	3.10 (2.31)	4.24 (3.16)
Oxides of Nitrogen, NO _x ^c g/kw-hr, (g/lp-hr)	11.88 ^f (8.86)	11.19 (8.34)	5.26 (3.92)	7.31 (5.45)	6.79 (5.06)	7.89 (5.89)	6.88 (5.13)	7.38 (5.50)	7.90 (5.95)	8.62 (6.43)
Brake Specific Fuel Consump. ^d kg fuel/kw-hr, (lb fuel/lp-hr)	0.262 (0.431)	0.288 (0.473)	0.486 (0.799)	0.531 (0.873)	0.482 (0.792)	0.547 (0.900)	0.396 (0.651)	0.435 (0.715)	0.400 (0.657)	0.448 (0.737)
Test Cycle	7-mode	Transient	7-mode	Transient	7-mode	Transient	7-mode	Transient	7-mode	Transient
Total Individual HC mg/kw-hr	100	130	67	110	32	66	Not Run	500	Not Run	220
Total Unburned Alcohols mg/kw-hr		Does Not Apply	2200	4900	950	890		2300		860
Total Aldehydes ^e mg/kw-hr	19	14	88	250	140	260		240		250
Total Phenols mg/kw-hr	Not Run	35	17	24	14	48		44		33
Total Particulate g/kw-hr, (g/lp-hr)	0.69 (0.52)	0.70 (0.52)	0.30 (0.23)	0.39 (0.30)	0.51 (0.38)	0.37 (0.27)		0.35 (0.26)		0.38 (0.28)
Sulfate, SO ₄ ^f mg/kw-hr, (% of Part.)	45 (6.5%)	38 (5.4%)	14 (4.6%)	16 (4.1%)	220 (43%)	98 (27%)		14 (4.0%)		89 (23%)
Soluble Organic Fraction (SOF) mg/kw-hr, (% of Part.)	200 (28%)	220 (32%)	200 (66%)	280 (73%)	70 (14%)	60 (16%)		190 (53%)		40 (11%)
BaP in SOF µg/kw-hr										
Ames Response (TA98) revertant/mg SOF										

^a Run with backpressure device engaged during idle and motoring.

^b HC value reported here is based on measurements by HFID. FID response is very low for unburned alcohols and other species of unregulated emissions.

^c 13-mode NO_x correction factor for intake humidity was computed but not applied.

^d Computed on the basis of measured diesel consumption and alcohol consumption combined.

^e Benzaldehyde was not included in the total composite value.

^f NO_x value is reduced to 10.89 g/kw-hr (8.12 g/lp-hr) when the intake humidity correction for NO_x is applied.

^g Phenols were determined from only selected modes without backpressure device at idle.

^h Average of data with and without backpressure device.

TABLE 15. SUMMARY OF COMPOSITE EMISSION RATES FROM THE VOLVO TD-100C DIESEL ENGINE AND THE VOLVO TD-100A DIESEL PILOT/ALCOHOL ENGINE

Composite Emission Rates	Engine Test Configuration											
	Diesel Volvo TD-100C		Methanol Volvo TD-100A		Methanol-Catalyst Volvo TD-100A		Ethanol Volvo TD-100A		Ethanol-Catalyst Volvo TD-100A		Ethanol+30% Water Volvo TD-100A	
Federal Test Procedure (FTP)	13-mode	Transient	13-mode	Transient	13-mode ^h	Transient ⁱ	13-mode	Transient	13 mode	Transient	13-mode	Transient
Hydrocarbon, HC ^b g/kw-hr, (g/hp-hr)	1.05 (0.78)	1.15 (0.85)	1.45 (1.08)	1.95 (1.45)	0.16 (0.12)	0.22 (0.16)	1.65 (1.23)	2.27 (1.69)	0.60 (0.45)	0.63 (0.47)	1.89 (1.41)	Not Run
Carbon Monoxide, CO g/kw-hr, (g/hp-hr)	3.18 (2.37)	4.04 (3.01)	9.55 (7.12)	10.29 (7.67)	0.83 (0.62)	3.74 (2.79)	10.53 (7.85)	12.89 (9.61)	3.10 (2.31)	4.24 (3.16)	9.99 (7.45)	
Oxides of Nitrogen, NO _x ^c g/kw-hr, (g/hp-hr)	11.88 ^f (8.86)	11.19 (8.34)	5.26 (3.92)	7.31 (5.45)	6.79 (5.06)	7.89 (5.89)	6.88 (5.13)	7.38 (5.50)	7.98 (5.95)	8.62 (6.43)	4.46 (3.32)	
Brake Specific Fuel Consump. ^d kg fuel/kw-hr, (lb fuel/hp-hr)	0.262 (0.431)	0.288 (0.473)	0.486 (0.799)	0.531 (0.873)	0.482 (0.792)	0.547 (0.900)	0.396 (0.651)	0.435 (0.715)	0.400 (0.657)	0.448 (0.737)	0.495 (0.814)	
Test Cycle	7-mode	Transient	7-mode	Transient	7-mode	Transient	7-mode	Transient	7-mode	Transient	7-mode	Transient
Total Individual HC mg/kw-hr	100	130	67	180	32	66	Not Run	600	Not Run	220	220	Not Run
Total Unburned Alcohols mg/kw-hr	Does Not Apply	Does Not Apply	2200	4900	950	890		2300		480	860	
Total Aldehydes ^e mg/kw-hr	19	14	88	250	140	260		240		250	91	
Total Phenols mg/kw-hr	Not Run	35	17	24	14	48		44		33	Not Run	
Total Particulate g/kw-hr, (g/hp-hr)	0.69 (0.52)	0.70 (0.52)	0.30 (0.23)	0.39 (0.30)	0.51 (0.38)	0.37 (0.27)		0.35 (0.26)		0.38 (0.28)	0.33 (0.243)	
Sulfate, SO ₄ ^g mg/kw-hr, (% of Part.)	45 (6.5%)	38 (5.4%)	14 (4.6%)	16 (4.1%)	220 (43%)	98 (27%)		14 (4.0%)		89 (23%)	17 (5.2%)	
Soluble Organic Fraction (SOF) mg/kw-hr, (% of Part.)	200 (28%)	220 (32%)	200 (66%)	280 (73%)	70 (14%)	60 (16%)		190 (53%)		40 (11%)	190 (58%)	
BaP in SOF µg/kw-hr												
Ames Response (TA98) revertant/mg SOF												

^a Run with backpressure device engaged during idle and motoring.

^b HC value reported here is based on measurements by HFID. PID response is

very low for unburned alcohols and other species of unregulated emissions

^c 13-mode NO_x correction factor for intake humidity was computed but not

applied

^d Computed on the basis of measured diesel consumption and alcohol consumption

combined

^e Benzaldehyde was not included in the total composite value

^f NO_x value is reduced to 10.89 g/kw-hr (8.12 g/hp-hr) when the intake

humidity correction for NO_x is applied.

^g Phenols were determined from only selected modes

^h Without backpressure device at idle

ⁱ Average of data with and without backpressure device

Future work in the alcohol area will include the testing of a Volkswagen that is fueled exclusively by methanol and compared to the results from a Volkswagen fueled exclusively by gasoline. It is also hoped that an Escort designed for use with 100% methanol can be obtained such that its emissions data can be compared to the data discussed above. The Volkswagen will be tested and its emissions analyzed by mass spectroscopy so that a broad characterization, in a qualitative sense, can be made between the emissions from these gasoline-fueled and methanol-fueled engines.

E. Nitrosamines

Nitrosamines are a group of compounds that take the general form of $R_2N=NO$. Nitrosamines have been described as among the most broadly acting and the most potent carcinogens. More than 100 nitrosamines have been tested for carcinogenic activity and most of them have induced tumors in rats. A smaller number have been tested in hamsters, mice, or guinea pigs, and again most of those tested have been carcinogenic. As a result nitrosamines are considered to be very hazardous to humans because of their assumed carcinogenicity in humans.

Very little monitoring of roadside nitrosamines has been performed. However, what limited work has been done to date has shown instances of nitrosamines up to approximately one microgram per cubic meter. It appears as though these roadside levels are mobile source related. However, only two sources of nitrosamines have been confirmed, as well as one possible source. The confirmed sources included are 1) crankcase emissions from heavy-duty Diesels, and 2) automobile interior emissions (20, 21, 22, 23, 24). The possible source of nitrosamines is indicated by one datum point that showed nitrosamines may be present in heavy-duty Diesel exhaust. This latter datum point is, as of yet, unconfirmed.

The work on nitrosamines from heavy-duty Diesel crankcases indicated that the most likely source for these nitrosamines was the oil additives that are used for purposes of improving the performance characteristics of the oil. There is a clear association between the nitrosamine emissions from an engine using new oil and the level of nitrosatable amines that is measured

by a bench procedure. There was also an influence due to engines (probably those factors influencing NOx emission rates) as well as a probable association with the amount of time that the oil is used. However, this latter association has not been totally confirmed. There would also be nitrosamines from light-duty Diesel blowby. A number of different sources have indicated that neither nitrosamines nor nitrosamine precursors are emitted in the exhaust of gasoline vehicles. It is very likely that gasoline engines would also have nitrosamines in their blowby. However, the blowby from gasoline vehicles is currently recirculated through the engine.

The significance of the roadside concentrations is not easy to estimate very accurately, due to the lack of models specifically tailored for that purpose and the lack of adequate nitrosamine roadside monitoring data. However, some very rough approximations have shown that the number of cancer incidences per year may not be insignificant for the exposure levels detected.

Also, some recent EPA work has shown nitrosamines to be present in vehicle interiors (23). In the vehicle interior work, 56 vehicles were sampled for nitrosamines. Of these 56 vehicles, detectable levels of nitrosamines were found in 47. Concentrations of detectable nitrosamines in these vehicles' interiors ranged from 0.01 to 0.16 micrograms per cubic meter. The test results indicated an N-dimethyl nitrosamine (NDMA) dependence on mileage and time with NDMA levels decreasing slightly with time and mileage. Also, an NDMA dependence on temperature was observed, with higher temperatures giving higher levels of NDMA. The levels of NDMA in vehicles during operation was observed to decrease somewhat, but they rebounded quite rapidly after operation. Also similar levels of NDMA in vehicles were observed after either an overnight soak or for vehicles closed for only a short time. Nitrosamines were found in passenger cars, stationwagons, passenger and cargo vans, pick-up trucks, as well as in new and used heavy-duty trucks. Nitrosamines were not detected in motor homes. A very rough analysis was made and it was observed that on the average, the daily intake of nitrosamines from vehicle interiors would be less than the amount contained in a can of beer (before nitrosamines in beer were regulated to lower levels) and more than the level found in a strip of bacon (bacon is currently regulated for nitrosamine content).

F. Identification of Types of Compounds Responsible for Ames Test Activity in Diesel Particulates

Many investigators including those in EPA, the automotive industry, and private investigators such as those at the University of California at Berkeley, are conducting studies to identify the compounds responsible for the Ames test activity of Diesel particulate extract. These researchers have spent effort in separating the methylene chloride extract of Diesel particulates by high pressure liquid chromatography (HPLC). Three major fractions have been obtained by HPLC: non-polar, moderately polar (transition), and highly polar.

The non-polar fraction consists of aliphatic and polynuclear aromatic hydrocarbons (many of them alkyl substituted) which were responsible for only a portion of the Ames test activity.

The transition and polar fractions accounted for most of the Ames test activity. About 50% by weight of the material in the transition fraction consisted of various oxygenated polynuclear aromatic hydrocarbons (including hydroxy, ketone, carboxaldehyde, quinone, acid anhydride, and nitro compounds). The polar fraction consisted of carboxylic acid polynuclear aromatic hydrocarbons which also have significant Ames test activity (25).

Appendix 1 (26) lists the compounds which have been identified so far in the joint project on Diesel particulate fractions being conducted by Ford Motor Company and EPA.

Appendix 2 lists the compounds which have been identified by Sklarew et al. of Battelle Northwest.

G. Development of Method to Collect/Characterize Gas-phase Hydrocarbons

OMSAPC has been concerned about the potential hazard of automobile exhaust hydrocarbons for several years. As such, OMSAPC has been very interested in the development of a method to collect artifact-free samples of gas phase

hydrocarbons in motor vehicle exhaust for bioassay testing. EPA/ESRL has evaluated both a filter cartridge and a condensate method and ECTD has done some limited gas phase sampling and analysis.

Preliminary tests performed by ESRL have been done with a method involving filtering the exhaust particulates and then condensing components in the gas stream. The condensate appeared to have low Ames test activity. If the filter upstream of the condenser were removed, the condensate contained some Diesel particulate and had somewhat higher Ames test activity.

The filter cartridge method involved passing a gas stream sample after a conventional particulate filter through a cartridge or bed of treated XAD-2 resin. After the gas stream was passed through the XAD-2, the hydrocarbons adsorbed onto the XAD-2 were removed from the resin by methylene chloride extraction. The lower molecular weight hydrocarbons (e.g. below C-10) were sufficiently volatile that they were probably lost during the extraction. However, hydrocarbons above C-10 were retained and could then be subject to the Ames test. Since the conventional particulate filter generally retained hydrocarbon compounds above C-15, the XAD-2 traps could provide a good method to collect hydrocarbons in the C-10 to C-15 range (25).

A very preliminary result of Ames testing on the gas phase hydrocarbon collected by this method for a VW Diesel Rabbit showed that the activity may be low compared to that of the particulate.

ECTD/TAEB has done some work wherein a light-duty Diesel vehicle was used to load a large filter with particulate. The volatile organic material was then driven off by heating the filter to 1000°F which is slightly below the ignition point of carbon. These "organic free" filters were then put downstream of a particulate filter in a stream of Diesel exhaust. Thus, presumably the "organic free" filters would be subjected only to the gas phase hydrocarbons of the exhaust stream. The carbon on the downstream filter provided a media for collection of the hydrocarbons. The preliminary results of this work indicated 1) collection of some hydrocarbon material on the filter, and 2) some apparently significant Ames test activity associated with the hydrocarbons thus collected (27).

H. Ames Testing

ECTD has conducted a number of experiments wherein the emissions were sampled and subjected to the Ames bioassay test. One such study was with the Diesel fuels project (discussed in section IV D 1.) and these data are summarized in Tables 16 and 17. These data seemed to show little effect from fuel nitrogen levels when the nitrogen was introduced in the form of isoquinoline. There also appeared to be a trend towards a decrease in activity when olefins were introduced to the base fuel. The heavy ends indicated a possible trend towards increasing Ames test activity and also the same could possibly be said for the cetane improver as it appeared to increase the Ames test activity. The other trend appeared to be towards an increase in Ames test activity with the use of aromatics. This included the heavy aromatic naptha (HAN) as well as the individual aromatics (15).

These findings tend to be corroborated with the preliminary results reported by Sklarew from Battelle Northwest. Sklarew et al. rather extensively characterized Diesel particulate extract from filters provided by ECTD from the Southwest Research Institute fuels project discussed above. These samples were taken when the vehicle was operated on 1) base fuel, 2) base fuel + isoquinoline (0.05% N), 3) base fuel + isoquinoline (0.10% N), and 4) base fuel + HAN + cetane improver. They concluded that there was a slight but positive correlation between higher aromatic content in the parent fuel and mutagenicity of the chemical fractions from combustion particulates of that fuel. No correlation was found by them between increased mutagenicity and the nitrogen content (from isoquinoline) of the parent Diesel fuel. However, they also observed that the fuel with isoquinoline added prior to combustion appeared to have lower mutagenic activity than the same fuel without isoquinoline. Their preliminary data suggested that the high aromatic Diesel fuels gave rise to higher concentrations of indirect acting mutagens in the aromatic hydrocarbons, moderately polar or neutrals and highly polar neutrals than do the low aromatic Diesel fuels (28).

The other set of Ames test data that has been recently analyzed was that from the Volvo testing wherein the dual fueled Volvo (which employed Diesel

TABLE 16. SUMMARY OF AMES BIOASSAY ANALYSIS OF ORGANIC SOLUBLES FROM PARTICULATE MATTER COLLECTED DURING FTP

Fuel Code	Description	RLI-16 Activation	Model Predicted Mean Slope, revertants/ μ g extract				
			TA-1535	TA-1537	TA-1538	TA-98	TA-100
EM-395-F	base	No	0.0	0.2	0.7	3.2	3.9
		Yes	0.0	0.3	0.4	0.9	1.9
EM-404-F	base + isoquinoline (0.05% N)	No	0.0	0.7	1.7	3.3	5.1
		Yes	0.1	0.5	1.0	3.0	1.9
EM-405-F	base + isoquinoline (0.10% N)	No	0.0	0.1	0.5	1.9	5.5
		Yes	0.2	1.1	0.9	0.8	1.3
EM-430-F	base + shale oil cut	No	0.3	0.2	0.6	1.3	4.9
		Yes	0.0	0.2	0.7	1.0	1.9
EM-434-F	base + "HAN"	No	0.0	0.7	1.7	3.7	6.9
		Yes	0.1	0.5	1.1	1.1	2.2
EM-438-F	base + olefins	No	0.0	0.1	0.3	0.8	3.0
		Yes	0.0	0.2	0.5	1.3	1.2
EM-448-F	base + light ends	No	0.0	0.4	0.9	4.1	3.3
		Yes	0.1	1.3	0.7	0.9	1.4
EM-401-F	JP-7	No	0.0	0.2	1.4	3.0	--
		Yes	0.1	0.3	0.9	3.3	1.4
EM-460-F	base + individual aromatics	No	0.0	0.7	1.7	3.5	8.7
		Yes	0.1	0.4	0.9	2.9	2.6
EM-461-F	base + heavy ends	No	0.0	0.3	1.2	3.6	6.6
		Yes	0.1	0.5	1.0	2.7	2.3
EM-463-F	EM-434-F + cetane improver	No	0.0	0.7	1.7	5.7	14.0
		Yes	0.1	0.6	0.9	2.5	2.4

TABLE 17. AMES BIOASSAY ANALYSIS RESULTS IN REVERTANTS PER
DISTANCE DURING FTP

Fuel Code	Description	RLI-16 Activation	Model Predicted Mean Slope, 10^3 revertants/km ^a				
			TA-1535	TA-1537	TA-1538	TA-98	TA-100
EM-395-F	base	No	0.0	7.	25.	112.	137.
		Yes	0.0	11.	14.	32.	67.
EM-404-F	base + isoquinoline (0.05% N)	No	0.0	16.	40.	77.	119.
		Yes	2.	12.	23.	70.	44.
EM-405-F	base + isoquinoline (0.10% N)	No	0.0	3.	13.	50.	145.
		Yes	5.	29.	24.	21.	34.
EM-430-F	base + shale oil cut	No	7.	5.	14.	30.	112.
		Yes	0.0	5.	16.	23.	43.
EM-434-F	base + "HAN"	No	0.0	18.	43.	93.	173.
		Yes	3.	13.	28.	28.	55.
EM-438-F	base + olefins	No	0.0	2.	6.	17.	65.
		Yes	0.0	4.	11.	28.	26.
EM-448-F	base + light ends	No	0.0	11.	25.	116.	93.
		Yes	3.	37.	20.	25.	40.
EM-401-F	JP-7	No	0.0	5.	36.	77.	--
		Yes	3.	8.	23.	85.	36.
EM-460-F	base + individual aromatics	No	0.0	18.	44.	90.	223.
		Yes	3.	10.	23.	74.	67.
EM-461-F	base + heavy ends	No	0.0	8.	33.	100.	184.
		Yes	3.	14.	28.	75.	64.
EM-463-F	EM-434-F + cetane improver	No	0.0	22.	53.	176.	433.
		Yes	3.	19.	28.	77.	74.

^a calculation incorporates particulate mass rates based on 47 mm Pallflex filters, percent organic solubles extracted from Pallflex "20x20" filters, and data in Table 23.

fuel pilot injection and alcohol main injection) was tested and compared against a baseline pure Diesel Volvo engine.

Table 18 shows that the change between the methanol and methanol plus catalyst case resulted in a 20% decrease in particulate and an 82% decrease in organics with use of the catalyst. However, the use of the catalyst also resulted in a very dramatic increase in the revertants per plate as seen in the first column of data. This increase was between about 300 and 5,400%. However, when the accompanying reduction in organics was incorporated into the data, the increase in revertants per kilowatt hour column was not nearly as dramatic. However, there was still generally an increase per kilowatt hour associated with the methanol with catalyst configuration. Basically the same trend was exhibited by the ethanol and ethanol catalyst comparison.

Table 19 shows the data from the pure Diesel fueled baseline engine compared against the dual-fueled engine using methanol. Both transient and the steady state data are presented. Some preliminary conclusions can be made from these new data. For example, the Ames test activity results from the dual fueled engine using methanol tested over the transient cycle were generally lower than the baseline/pure Diesel fueled engine. However, the dual fueled engine using methanol and Diesel fuel seemed to show higher activity than the baseline engine over the 13 mode cycle. This apparent discrepancy may be explained by looking at the modal data which showed that the heavier loaded modes tend to result in higher Ames test activity than lightly loaded modes (an interesting observation in-and-of itself). This trend was much more pronounced for the dual fueled engine using methanol than for the pure Diesel fuel engine. This, combined with the fact that the transient cycle is more lightly loaded than the 13 mode test, could account for the above mentioned apparent conflict. The steady state runs (13 mode) with the dual fueled engine using methanol and Diesel fuel with the catalyst tended to have slightly higher specific activity in revertants per micrograms of extract but lower revertants per kilowatt hour responses than the same engine but without the catalyst. This is in some conflict with the earlier data as presented in Table 18 wherein the transient cycle comparison showed both the specific activity and the revertants per kilowatt hour to be

Table 18

Average Percent Change Between Two Variables
Dual Fueled Volvo TD100A - Transient Composite Test Cycle

Variable A Variable B	METHANOL METHANOL W/CAT		ETHANOL ETHANOL W/CAT		METHANOL ETHANOL		METHANOL W/CAT ETHANOL W/CAT	
	Rev/Plate-ug	Rev/kW hr	Rev/Plate-ug	Rev/kW hr	Rev/Plate-ug	Rev/kW hr	Rev/Plate-ug	Rev/kW hr
Particulate g/kW-hr	-20%	+8%	-13%	-36%	+17%	-25%		
Organics g/kW-hr	-82%	-79						
Ames Data								
TA 98 No Act.	10012	99%	899%	115%	126%	43%	110%	58%
TA 98 Act.	457	0	534	36	125	42	146	86
TA 100 No Act.	285	-30	165	-43	169	72	40	4
TA100 Act.	745	53	1041	144	163	68	186	116
TA1535 No Act.	None*	None*	100	100	None*	None*	225	100
TA1535 Act.	1050	125	25	-67	200	88	-61	-63
TA1537 No Act.	4463	694	7608	1573	208	85	470	325
TA1537 Act.	1473	194	18699	3883	214	105	1797	1312
TA1538 No Act.	5402	331	708	73	242	114	-50	61
TA1538 Act.	296	-29	2809	523	58	0**	861	621

$$\text{Average Percent Change} = (100) \frac{B_1 - A_1 + \frac{B_2 - A_2}{2}}{A_1}$$

Where: A₁ = Results from Variable A tested on 2/11/80
 B₁ = Results from Variable B tested on 2/11/80
 A₂ = Results from Variable A tested on 1/27/81
 B₂ = Results from Variable B tested on 1/17/81

* "None" Indicates no change in the two variables.
 ** "0" Indicates no or negligible Ames test response.

Table 19

Average Percent Change Between Two Variables
Dual Fueled Volvo TD100A

Variable A → Variable B →	Diesel-transient		Diesel 13-Mode		Methanol 13-Mode		Diesel 13-Mode	
	Methanol-transient		Methanol 13-Mode		Methanol + Catalyst 13-Mode		Ethanol + H ₂ O - 13-Mode	
Particulate g/kW hr	-44%		-57%		+70%		-52%	
Organics g/kW hr	+27%		-0%		-65%		-5%	
Ames Data								
TA 98 No Act.	-81%	-76%	+156%	-43%	+156%	-80%	-56%	-56%
TA 98 ACT.	-76%	-69%	+367%	-21%	+367%	-73%	0%	-08%
TA 100 No Act.	-81%	-75%	--	+13%	--	-60%	--	--
TA 100 Act.	-65%	-54%	3%	+44%	+3%	-50%	+60%	+61%
TA1535 No Act.	0%	0%	0%	0%	0%	0%	0%	0%
TA1535 Act.	0%	0%	0%	0%	0%	0%	0%	-52-
TA1537 No Act.	-94%	-91%	+50%	0%	+50%	-33%	-67%	-67%
TA1537 Act.	-90%	-86%	-17%	0%	-17%	-60%	-100%	-100%
TA1538 No Act.	-89%	-85%	0%	-33%	0%	-75%	-83%	-83%
TA1538 Act.	-83%	-79%	0%	+188%	0%	0%	-38%	-38%

higher with the catalyst than without the catalyst. Therefore, one would conclude that the test cycle is very important when analyzing the Ames test data from those engines (18).

V.

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VI. Appendixes

Appendix 1

Compounds Identified in Diesel Particulate Emissions

This Appendix is reprinted directly from the following publication:

Dennis Schuetzle, Frank S.C. Lee, and Thomas J. Prater, Ford Motor Co., and Silvester B. Tejada, EPA, "The Identification of Polynuclear Aromatic Hydrocarbon Derivatives in Mutagenic Fractions of Diesel Particulate Extracts", presented at the 10th Annual Symposium on the Analytical Chemistry of Pollutants, Dortmund, Germany, May 28-30, 1980 which was published in the "International Journal of Environmental Analytical Chemistry", 9, 93 (1981).

TABLE IV

RELATIVE ABUNDANCES OF PAH SPECIES IDENTIFIED BY
GC/MS (25m DEXSIL 300 CAPILLARY COLUMN) AND HRMS FOR THE PAH (α_1 , α_2)
HPLC FRACTIONS OF A DIESEL PARTICULATE EXTRACT (OL-1)

<u>Compounds</u>	<u>Formula</u>	¹ <u>Mass</u>	<u>Relative² Abundance</u>
Phenanthrene and Anthracene	C ₁₄ H ₁₀	178.078	0.27
Methyl (Phenanthrenes and Anthracenes)	C ₁₅ H ₁₂	192.094	0.54
Fluoranthene	C ₁₆ H ₁₀	202.078	0.41
Pyrene	C ₁₆ H ₁₀	202.078	0.41
Dihydro (Fluoranthenes and Pyrenes)	C ₁₆ H ₁₂	204.094	0.09
Dimethyl (Phenanthrenes and Anthracenes)	C ₁₆ H ₁₄	206.110	1.00
Benzofluorenes	C ₁₇ H ₁₂	216.094	0.67
Methylpyrenes	C ₁₇ H ₁₂	216.094	0.55
Benzyl naphthalenes	C ₁₇ H ₁₄	218.110	0.18
Trimethyl (Phenanthrenes or Anthracenes)	C ₁₇ H ₁₆	220.126	0.37
Cyclopentapyrene	C ₁₈ H ₁₀	226.078	0.47
Benzo(a) Anthracene(BaA), Chrysene, and Triphenylene	C ₁₈ H ₁₂	228.094	0.16
Diphenylbenzene	C ₁₈ H ₁₄	230.110	0.11
Methyl (BaA, Chrysene and Triphenylene)	C ₁₉ H ₁₄	242.110	0.42
Benzofluoranthenes	C ₂₀ H ₁₂	252.094	0.33
Benzo(e) Pyrene(BaP), Benzo(a) Pyrene(BaP) and Perylene	C ₂₀ H ₁₂	252.094	0.48
Methyl Benzofluoranthenes	C ₂₁ H ₁₄	266.110	0.13
Methyl (BaP, BaP, Perylene)	C ₂₁ H ₁₄	266.110	0.16
Benzo(g,h,i) Perylene and Anthanthrene	C ₂₂ H ₁₂	276.094	0.25
Coronene	C ₂₄ H ₁₂	300.094	0.06
Dibenzopyrenes	C ₂₄ H ₁₄	302.110	0.02

¹ Measured to within $\pm$ 10 ppm at 12K resolution.

² Abundance relative to dimethyl (phenanthrenes and anthracenes)

TABLE V

CHEMICAL COMPOSITION OF THE β - HPLC FRACTIONS OF A DIESEL PARTICULATE EXTRACT (NI-1)

COMPOUND	MASS		RELATIVE ABUNDANCE (FRACTION #)						
	Found	Theory	24	25	26	27	28	29	30
Anthanthrene or Isomers ($C_{22}H_{12}$)	276.097	276.094	0.181	0.009	-	-	-	-	-
Methyl Anthanthrene or Isomers ($C_{23}H_{14}$)	290.108	290.109	0.362	0.269	-	-	-	-	-
Coronene ($C_{24}H_{12}$)	300.092	300.094	0.121	0.159	1.000	0.480	0.293	0.073	-
Dibenzopyrene ($C_{24}H_{14}$) - 2 Isomers	302.106	302.109	0.481	0.097	0.068	0.128	0.202	0.174	-
Methyl Coronene ($C_{25}H_{14}$)	314.109	314.109	-	-	-	0.010	0.028	-	-
Hydroxy Coronene ($C_{24}H_{12}O$)	316.091	316.089	0.034	0.042	0.049	0.051	0.032	-	-
Cyclopentacorone or Cyclopentenodibenzopyrene ($C_{26}H_{14}$)	326.111	326.110	-	-	-	0.053	0.162	0.109	0.043

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TABLE VI

RELATIVE ABUNDANCE OF CHEMICAL SPECIES IDENTIFIED BY GC/MS (SP 2250 COLUMN) IN THE
TRANSITION (Y₁) HPLC FRACTION OF A DIESEL PARTICULATE EXTRACT-OL-I

COMPOUND	FORMULA	MASS	SCAN#	RELATIVE ABUNDANCE
2-Naphthalene Carboxaldehyde	C ₁₁ H ₈ O	156.061	660	0.035
1-Naphthalene Carboxaldehyde	C ₁₁ H ₈ O	156.061	673	0.059
Methyl Naphthalene Carboxaldehyde	C ₁₂ H ₁₀ O	170.073	779	0.062
Naphthalene Acetaldehyde	C ₁₂ H ₁₀ O	170.073	789	0.073
Naphthalene Acetaldehyde	C ₁₂ H ₁₀ O	170.073	795	0.015
Dimethyl Naphthalene Carboxaldehyde	C ₁₂ H ₈ O ₂	184.052	868	0.098
9-Fluorenone	C ₁₃ H ₈ O	180.058	881	1.000
Naphthalene Dicarboxaldehyde	C ₁₂ H ₈ O ₂	184.052	894	0.140
Phenanthrene or Anthracene	C ₁₄ H ₁₀	178.078	895	0.260
Naphthalene Dicarboxaldehyde	C ₁₂ H ₈ O ₂	184.052	925	0.047
Phenanthrone or Anthrone	C ₁₄ H ₁₀ O	194.073	941	0.110
Naphthalene Dicarboxaldehyde	C ₁₂ H ₈ O ₂	184.052	943	0.028
9-Anthrone	C ₁₄ H ₁₀ O	194.073	947	0.040
Trimethyl Naphthalene Carboxaldehyde	C ₁₄ H ₁₄ O	198.104	950	0.061
Phenanthrone or Anthrone	C ₁₄ H ₁₀ O	194.073	961	0.197
Trimethylnaphthalene Carboxaldehyde	C ₁₄ H ₁₄ O	198.104	965	0.062
Fluorene Carboxaldehyde	C ₁₄ H ₁₀ O	194.073	989	0.176
Methyl (Anthracene or Phenanthrene)	C ₁₅ H ₁₂	192.094	991	0.128
Methyl (Anthracene or Phenanthrene)	C ₁₅ H ₁₂	192.094	998	0.168
Fluorene Carboxaldehyde	C ₁₄ H ₁₀ O	194.073	1000	0.176
9-Xanthone	C ₁₃ H ₈ O ₂	196.052	1004	0.039
Trimethyl Naphthalene Carboxaldehyde	C ₁₄ H ₁₄ O	198.104	1010	0.031
Fluorene Carboxaldehyde	C ₁₄ H ₁₀ O	194.073	1021	0.134
Methyl (Anthracene or Phenanthrene)	C ₁₅ H ₁₂	192.094	1022	0.136

COMPOUND	FORMULA	MASS	SCAN#	RELATIVE ABUNDANCE
Trimethyl Naphthalene Carboxaldehyde	C ₁₄ H ₁₄ O	198.104	1040	0.030
2-Methyl 9-Anthrone	C ₁₅ H ₁₂ O	208.089	1057	0.241
Methyl (Anthrone or Phenanthrone)	C ₁₅ H ₁₂ O	208.089	1077	0.144
Dimethyl (Anthracene or Phenanthrene)	C ₁₆ H ₁₄	206.109	1090	0.121
9,10 Phenanthrene Quinone	C ₁₄ H ₁₀ O ₂	208.052	1094	0.063
(Phenanthrene or Anthracene) Quinone	C ₁₄ H ₁₀ O ₂	208.052	1105	0.070
Dimethyl (Anthracene or Phenanthrene)	C ₁₆ H ₁₄	206.109	1111	0.057
9,10 Anthracene Quinone	C ₁₄ H ₁₀ O ₂	208.052	1122	0.231
(Phenanthrene or Anthracene) Quinone	C ₁₄ H ₁₀ O ₂	208.052	1142	0.044
Pyrene	C ₁₆ H ₁₀	202.078	1157	0.237
Methyl 9,10 Phenanthrene Quinone	C ₁₅ H ₁₀ O ₂	222.068	1171	0.180
Unknown	C ₁₅ H ₈ O	204.057	1172	1.041
Trimethyl (Anthracene or Phenanthrene)	C ₁₇ H ₁₆	220.125	1175	0.020
Methyl 9,10 (Anthracene or Phenanthrene) Quinone	C ₁₅ H ₁₀ O ₂	222.068	1193	0.092
Trimethyl (Anthracene or Phenanthrene)	C ₁₇ H ₁₆	220.125	1199	0.095
Fluoranthene	C ₁₆ H ₁₀	202.078	1205	0.190
Thioxanthone	C ₁₃ H ₈ OS	212.030	1208	0.057
Trimethyl (Anthracene or Phenanthrene)	C ₁₇ H ₁₆	220.125	1217	0.046
Methyl 9,10 Anthracene Quinone	C ₁₅ H ₁₀ O ₂	222.068	1231	0.095
Pyrone	C ₁₆ H ₁₀ O	218.073	1235	0.087
Thioxanthone	C ₁₃ H ₈ OS	212.030	1237	0.061
(Phenanthrene or Anthracene) Carboxaldehyde	C ₁₅ H ₁₀ O	206.073	1249	0.354
9-Thioxanthone	C ₁₃ H ₈ OS	212.030	1251	0.269
(Phenanthrene or Anthracene) Carboxaldehyde	C ₁₅ H ₁₀ O	206.073	1260	0.294
Fluoranthone or Pyrone	C ₁₆ H ₁₀ O	218.073	1270	0.041
Fluoranthone or Pyrone	C ₁₆ H ₁₀ O	218.073	1284	0.043
Methyl (Phenanthrene or Anthracene) Carboxaldehyde	C ₁₆ H ₁₂ O	220.089	1316	0.085

COMPOUND	FORMULA	MASS	SCAN#	RELATIVE ABUNDANCE
Unknown		226 ²	1318	0.024
Methyl (Phenanthrene or Anthracene) Carboxaldehyde	C ₁₆ H ₁₂ O	220.089	1338	0.188
Methyl Pyrene	C ₁₇ H ₁₂	216.094	1338	0.024
Pyrene Quinone	C ₁₆ H ₈ O ₂	232.052	1338	0.024
Methyl (Phenanthrene or Anthracene) Carboxaldehyde	C ₁₆ H ₁₂ O	220.089	1355	0.126
Methyl Fluoranthene	C ₁₇ H ₁₂	216.094	1357	0.221
Fluoranthene Quinone	C ₁₆ H ₈ O ₂	232.052	1357	0.023
Methyl (Phenanthrene or Anthracene) Carboxaldehyde	C ₁₆ H ₁₂ O	220.089	1369	0.094
Dimethyl (Phenanthrene or Anthracene) Carboxaldehyde	C ₁₇ H ₁₄ O	234.104	1413	0.057
Pyrene or Fluoranthene Carboxaldehyde	C ₁₇ H ₁₀ O	230.073	1415	0.409
Dimethyl (Phenanthrene or Anthracene) Carboxaldehyde	C ₁₇ H ₁₄ O	234.104	1440	0.051
Benzo(d,h) Anthrone	C ₁₇ H ₁₀ O	230.073	1450	0.073
Dimethyl (Phenanthrene or Anthracene) Carboxaldehyde	C ₁₇ H ₁₄ O	234.104	1462	0.027
(Benzo(a) anthracene, Chrysene or Triphenylene) Carboxaldehyde	C ₁₉ H ₁₂ O	256.089	1499	0.032
(Benzo(a) anthracene, Chrysene or Triphenylene) Carboxaldehyde	C ₁₉ H ₁₂ O	256.089	1518	0.028
(Benzo(a) anthracene, Chrysene or Triphenylene) Carboxaldehyde	C ₁₉ H ₁₂ O	256.089	1523	0.028
(Benzo(a) anthracene, Chrysene or Triphenylene) Carboxaldehyde	C ₁₉ H ₁₂ O	256.089	1536	0.032
1-Nitro Pyrene	C ₁₆ H ₉ NO ₂	247.063	1624	0.027

¹The relative abundance of 9-Fluorenone is arbitrarily given a value of 1.000.

²Mass accuracy is poor due to low ion abundance, therefore, exact empirical formula is difficult to establish.

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TABLE VII

A COMPARISON OF THE RELATIVE ABUNDANCES OF PAH DERIVATIVES
IDENTIFIED BY DIRECT PROBE HRMS AND GC/MS FOR THE
TRANSITION (γ_1) HPLC FRACTION OF A DIESEL PARTICULATE EXTRACT (OL-1)

POSSIBLE COMPOUNDS ¹	FORMULA	MASS	RELATIVE ABUNDANCE		
			HRMS	GC/MS ²	HRMS-GC/MS
9-Fluorenone	$C_{13}H_8O$	180.058	1.00	1.00	0.00
Hydroxy Fluorene*	$C_{13}H_{10}O$	182.073	0.15	0.00	0.15*
Naphthalene Dicarboxaldehyde	$C_{12}H_8O_2$	184.052	0.29	0.32	-0.03
Methyl (Anthracene or Phenanthrene)	$C_{15}H_{12}$	192.094	0.45	0.43	0.02
(Anthrone or Phenanthrone Fluorene Carboxaldehyde Methyl Fluorenone Hydroxy (Anthracene or Phenanthrene)*	$C_{14}H_{10}O$	194.073	0.96	0.83	0.13*
Fluorene Quinone 9-Xanthone Hydroxy Fluorenone*	$C_{13}H_8O_2$	196.052	0.66	0.04	0.62*
Hydroxy Xanthene*	$C_{13}H_{10}O_2$	198.068	0.30	0.00	0.30*
Dihydroxy Fluorene*					
Trimethyl Naphthalene Carboxaldehyde	$C_{14}H_{14}O$	198.104	0.29	0.19	0.10
Pyrene or Fluoranthene	$C_{16}H_{10}$	202.078	0.37	0.43	-0.05
Unknown	$C_{15}H_8O$	204.057	0.80	1.04	-0.24
Anthracene or Phenanthrene (Carboxaldehyde)	$C_{15}H_{10}O$	206.073	0.76	0.65	0.11
(Phenanthrene or Anthracene) Quinone	$C_{14}H_8O_2$	208.052	0.39	0.41	-0.02
Methyl (Anthrone or Phenanthrone)	$C_{15}H_{12}O$	208.089	0.35	0.39	-0.04
Thioxanthone	$C_{13}H_8OS$	212.030	0.47	0.39	0.08
Methyl Naphthalene Dicarboxylic Acid Anhydride: Hydroxy Xanthone	$C_{13}H_8O_3$	212.047	0.39	0.00	0.39*

POSSIBLE COMPOUNDS	FORMULA	MASS	RELATIVE ABUNDANCE		
			HRMS	GC/MS	HRMS-GC/MS
Fluoranthone or Pyrone	$C_{16}H_{10}O$	218.073	<0.15	0.17	-0.02
Methyl (Anthrone or Phenanthrene) (Dihydropyrone or Dihydrofluoranthene)	$C_{16}H_{12}O$	220.089	0.60	0.59	0.01
Aceanthrone or Acephenanthrone					
Methyl (Anthracene or Phenanthrene) Quinone	$C_{15}H_{10}O_2$	222.068	0.39	0.37	0.01
Unknown					
Dimethyl (Phenanthrone or Anthrone)	$C_{16}H_{14}O$	222.104	0.76	-	0.76*
Dimethyl Hydroxy (Phenanthrene or Anthracene)* Trimethyl Fluorenone					
Dihydroxy Methyl (Anthracene or Phenanthrene)*	$C_{15}H_{12}O_2$	224.084	0.44	-	0.44*
Hydroxy Nitro Fluorene*	$C_{13}H_9NO_3$	227.058	0.18	-	0.18*
(Pyrene or Fluoranthene) Carboxaldehyde Benzo(d,h) Anthrone	$C_{17}H_{10}O$	230.073	0.48	0.52	-0.04
Dimethyl (Anthracene or Phenanthrene) Carboxaldehyde; Unknown*	$C_{17}H_{14}O$	234.104	0.49	0.14	0.35*
Dihydrodihydroxy (Pyrene or Fluoranthene)*	$C_{16}H_{12}O_2$	236.084	0.30	-	0.30*
Hydroxy Trimethyl (Anthracene or Phenanthrene)*	$C_{17}H_{16}O$	236.120	0.18	-	0.18*
Nitro Methyl (Anthracene or Phenanthrene)*	$C_{15}H_{11}NO_2$	237.079	0.14	-	0.14*

¹ Those species that were not eluted in the GC/MS procedure but may be present based upon HRMS relative abundance values are designated by a star*

² Error in relative abundance values are $\pm 7\%$.

GC/MS identifications for this fraction are presented in Table VI.

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TABLE VIII

RELATIVE ABUNDANCE OF CHEMICAL SPECIES IDENTIFIED BY GC/MS (DEXSIL 300) IN THE GC/MS ANALYSIS OF A TRANSITION (Y₂) HPLC FRACTION OF A DIESEL PARTICULATE EXTRACT (OL-1)

Compound	Formula	Mass	Scan #	Relative Abundance
9-Fluorenone	C ₁₃ H ₈ O	180.058	719	0.157
Methyl Fluorenone	C ₁₄ H ₁₀ O	194.073	758	0.069
Methyl Fluorenone	C ₁₄ H ₁₀ O	194.073	787	0.041
Methyl Fluorenone	C ₁₄ H ₁₀ O	194.073	801	0.046
1 Naphtho (c,d) Pyrone	C ₁₂ H ₈ O ₂	184.052	808	0.105
Dimethyl Naphthalene Carboxaldehyde	C ₁₃ H ₁₂ O	184.089	846	0.040
Anthrone or Phenanthrone	C ₁₄ H ₁₀ O	194.073	853	0.175
Naphtho, 2-3-B-Furan-4,9-dione	C ₁₂ H ₆ O ₃	198.032	862	0.099
Naphthalene Dicarboxaldehyde	C ₁₂ H ₈ O ₂	184.052	863	0.054
Fluorene Quinone	C ₁₃ H ₈ O ₂	196.052	876	0.033
Fluorene Quinone	C ₁₃ H ₈ O ₂	196.052	888	0.040
9-Xanthone	C ₁₃ H ₈ O ₂	196.052	900	0.073
Unknown	C ₁₂ H ₁₀ O ₃	202.064	901	0.037
Fluorene Quinone	C ₁₃ H ₈ O ₂	196.052	904	0.133
Unknown	C ₁₂ H ₁₀ O ₃	202.064	912	0.030
Naphthalene Dicarboxylic Acid Anhydride	C ₁₂ H ₆ O ₃	198.032	918	1.000
(Phenanthrene or Anthracene) Quinone	C ₁₄ H ₈ O ₂	208.052	913	0.123
Methyl (Anthrone or Phenanthrone)	C ₁₅ H ₁₂ O	208.089	923	0.162
(Anthracene or Phenanthrene) Carboxaldehyde	C ₁₅ H ₁₀ O	206.073	928	0.020
Fluorene Quinone	C ₁₃ H ₈ O ₂	196.052	935	0.053
(Phenanthrene or Anthracene) Quinone	C ₁₄ H ₁₀ O ₂	208.052	948	0.064
Methyl Naphthalene Dicarboxylic Acid Anhydride	C ₁₃ H ₈ O ₃	212.047	970	0.123
Methyl Fluorene Quinone	C ₁₄ H ₁₀ O ₂	210.068	973	0.102
Methyl Fluorene Quinone	C ₁₄ H ₁₀ O ₂	210.068	979	0.091
Methyl Fluorene Quinone	C ₁₄ H ₁₀ O ₂	210.068	995	0.005
Methyl Naphthalene Dicarboxylic Acid Anhydride	C ₁₃ H ₈ O ₃	212.047	980	0.111
Dimethyl Fluorene Quinone	C ₁₅ H ₁₂ O ₂	224.084	1010	0.043
Methyl Naphthalene Dicarboxylic Acid Anhydride	C ₁₃ H ₈ O ₃	212.047	1015	0.108
Dimethyl Fluorene Quinone	C ₁₅ H ₁₂ O ₂	224.084	1030	0.035
Dimethyl Naphthalene Dicarboxylic Acid Anhydride	C ₁₄ H ₁₀ O ₃	226.064	1030	0.036
Dimethyl Fluorene Quinone	C ₁₅ H ₁₂ O ₂	224.084	1055	0.021
Dimethyl Naphthalene Dicarboxylic Acid Anhydride	C ₁₄ H ₁₀ O ₃	226.064	1059	0.120
Dimethyl Naphthalene Dicarboxylic Acid Anhydride	C ₁₄ H ₁₀ O ₃	226.064	1093	(2 Isomers) 0.012
(Fluoranthene or Pyrene) Quinone	C ₁₆ H ₈ O ₂	232.052	1148	0.026
Methyl (Pyrene or Fluoranthene) Quinone	C ₁₇ H ₁₀ O ₂	246.068	1210	0.005
Benzo(a)Anthracene, Chrysene or Triphenylene) Quinone	C ₁₈ H ₁₀ O ₂	258.068	1225	0.006
Benzo(a)Anthracene, Chrysene or Triphenylene) Quinone	C ₁₈ H ₁₀ O ₂	258.068	1235	0.012

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TABLE IX

A COMPARISON OF THE RELATIVE ABUNDANCES OF PAH DERIVATIVES IDENTIFIED BY DIRECT PROBE HRMS AND GC/MS FOR THE TRANSITION (Y₂) HPLC FRACTION OF A DIESEL PARTICULATE EXTRACT (OL-1)

Possible Compounds ¹	Formula	Mass	Relative Abundance		
			HRMS	GC/MS ^a	HRMS-GC/MS
9-Fluorenone	C ₁₃ H ₈ O	180.058	0.23	0.16	0.07
Hydroxy Fluorene*	C ₁₃ H ₁₀ O	182.072	0.30	-	0.30*
Naphthalene Dicarboxaldehyde	C ₁₂ H ₈ O ₂	184.052	0.11	0.12	-0.01
Dimethyl Naphthalene Carboxaldehyde	C ₁₃ H ₁₂ O	184.089	0.11	0.03	0.08
Anthrone or Phenanthrone	C ₁₄ H ₁₀ O	194.073	0.30	0.33	-0.03
Methyl Fluorenone					
9-Xanthone; Fluorene Quinone	C ₁₃ H ₈ O ₂	196.053	0.29	0.33	-0.03
Methyl Hydroxy Fluorene*	C ₁₄ H ₁₂ O	196.089	0.13	-	0.13*
Naphthalene Dicarboxylic Acid Anhydride	C ₁₂ H ₆ O ₃	198.031	1.00	1.00	-
Hydroxy Xanthene*	C ₁₃ H ₈ O ₂	198.067	0.38	-	0.38*
Dihydroxy Fluorene*					
Unknown	C ₁₂ H ₁₀ O ₃	202.064	0.05	0.07	-0.02
(Phenanthrene or Anthracene) Carboxaldehyde	C ₁₅ H ₁₀ O	206.073	0.03	0.02	0.01
(Phenanthrene or Anthracene) Quinone	C ₁₄ H ₈ O ₂	208.052	0.20	0.19	0.01
Methyl (Anthrone or Phenanthrone)	C ₁₅ H ₁₂ O	208.089	0.23	0.15	0.07*
Dimethyl Fluorenone					
Methyl Hydroxy (Anthracene or Phenanthrene)*					
Methyl Fluorene Quinone; Dihydroxy Anthracene*	C ₁₄ H ₁₀ O ₂	210.068	0.27	0.20	0.07*
Dimethyl Hydroxy Fluorene*	C ₁₅ H ₁₄ O	210.104	0.07	-	0.07*
Methyl Naphthalene Dicarboxylic Acid Anhydride	C ₁₃ H ₈ O ₃	212.047	0.36	0.34	0.02
Dihydroxy Methyl Fluorene*	C ₁₄ H ₁₂ O ₂	212.084	0.20	-	0.20*
Hydroxy Naphthalene Dicarboxylic Acid Anhydride*	C ₁₂ H ₆ O ₄	214.026	0.32	-	0.32*
Trihydroxy Fluorene*	C ₁₃ H ₁₀ O ₃	214.063	0.06	-	0.06*
Methyl (Anthracene or Phenanthrene) Quinone	C ₁₅ H ₁₀ O ₂	222.068	0.26	(?)	-
Anthracene or Phenanthrene) Dicarboxylic Acid Anhydride	C ₁₄ H ₈ O ₃	224.047	0.21	- (3)	-
Dimethyl Fluorene Quinone	C ₁₅ H ₁₂ O ₂	224.084	0.17	0.10	0.07
Dimethyl Naphthalene Dicarboxylic Acid Anhydride	C ₁₄ H ₁₀ O ₃	226.064	0.16	0.17	-0.01
Dihydroxy Methyl Fluorene*	C ₁₅ H ₁₄ O ₂	226.099	0.08	-	0.08*
Unknown*	C ₁₃ H ₈ O ₄	228.042	0.06	-	0.06*
Unknown*	C ₁₄ H ₁₂ O ₃	228.078	0.03	-	0.06*
Fluoranthene or Pyrene) Quinone	C ₁₆ H ₈ O ₂	232.052	0.04	0.03	0.01
Dihydroxy Dimethyl Anthracene*	C ₁₆ H ₁₄ O ₂	238.100	0.08	-	0.08*
Unknown*	C ₁₅ H ₁₄ O ₃	242.094	0.03	-	0.03*

Those species that were not eluted in the GC/MS procedure but may be present based upon HRMS relative abundance values are designated by a star*

GC/MS identifications for this fraction are presented in Table VIII.

Presence of compound not confirmed by GC/MS

Appendix 2

Compounds in Diesel Particulates Found by
Battelle Northwest (Reference 28)

Compound

Polycyclic Aromatic Hydrocarbons

Alkylated fluorenones

Alkylated phenols

Aliphatic acids

Methyl esters

Alkanones

Phenanthrenequinone

Benzoic Acid

Xanthen-9-one

Isobenzofuranone

N-aminopiperidine